

Spectroscopic Study of Photoreduction by the Fourth Harmonic of Nd:YAG Laser in a Liquid–Liquid Extraction System

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A new technique for the back-extraction using photoreduction by the fourth harmonic of Nd:YAG laser has been successfully demonstrated in a liquid–liquid extraction system composed of a 1-octanol solution of $\text{Eu}^{3+}(\text{TODGA})_n$ complex and water. The reduced product, Eu^{2+} ion, was stabilized by addition of 15-crown-5. The back-extraction process was investigated by laser-induced fluorescence spectroscopy. The results indicated slow diffusion of $\text{Eu}^{2+}(15\text{-crown-5})_m$ in the organic phase and fast transfer through the interface to the water.

Mutual separation of lanthanides (Ln) is well-known to be a hard task, because they are apt to have the same stable oxidation state, trivalent Ln (Ln^{3+}), and similar ionic radii. For several decades many researchers have studied liquid–liquid extraction as a wet-separation technique, where Ln^{n+} ions dissolved in water are separately extracted to organic solution by using various organic extractants. The efficiency of the separation in the extraction is greatly improved by using unstable oxidation states, e.g., Ce^{4+} , Eu^{2+} , Tb^{4+} , and Yb^{2+} , although strong oxidants or reductants are required. To decrease the harmful substances in the separation process, new oxidation and reduction techniques should be developed.

Ln^{3+} ions have absorption bands in UV regions that have been assigned to $4f\text{--}5d$ or charge-transfer transitions, whose excitation results in oxidation or reduction.¹ The valence of the selected Ln^{3+} ion can be arranged by photo-oxidation or -reduction with irradiation of narrow-band light, because the absorption bands are intrinsic to the ions. For instance, Hirai and Komasa have selectively photoreduced Eu^{3+} ion in organic solutions of Sm^{3+} , Eu^{3+} and Gd^{3+} complexes by a low-pressure mercury lamp (184.9 + 253.7 nm lines), and have separately extracted Eu^{2+} into water.² A laser, whose photon-flux is much larger than the lamp, also generates narrow-band light. Ion reduction by laser is more efficient than that by a lamp. Donohue have separated Eu from other elements of the Ln group in water by precipitation following ion reduction of Eu^{3+} by a UV pulse laser.³ However, there has been no report of solvent extraction using the ion reduction by laser as far as we know. In this paper, we newly developed a liquid–liquid extraction system combined with ion reduction by a UV pulse laser. The extraction process was investigated by laser-induced fluorescence (LIF) spectroscopy.

The liquid–liquid extraction system in this experiment was composed of a 1-octanol solution of $\text{Eu}^{3+}(\text{TODGA})_n$ complex ($\text{TODGA} = N,N,N',N'$ -tetraoctyldiglycolamide) and distilled water. The 1-octanol solution of $\text{Eu}^{3+}(\text{TODGA})_n$ was prepared by shaking equal volumes of a 2.7 M HCl solution containing 15 mM EuCl_3 (Wako Pure Chemical Industry) with a 1-octanol solution containing 50 mM TODGA for 30 min at 25 °C. After

centrifuging and separating the two solutions, the 1-octanol solution of $\text{Eu}^{3+}(\text{TODGA})_n$ was drawn up. The $\text{Eu}^{3+}(\text{TODGA})_n$ concentration in the 1-octanol solution was determined to be ca. 2.0 mM by $f\text{--}f$ transition absorbance at 394.2 nm. Finally, two milliliters of the 1-octanol solution of $\text{Eu}^{3+}(\text{TODGA})_n$ and the distilled water were introduced into a quartz cell with addition of 50 mM 15-crown-5 (15C5), and were shaken for 30 min to attain equilibrium. Here, the 15C5 ether, which can be dissolved in both 1-octanol and water, was used as the stabilizer and the spectral sensitization of the reduced Eu^{2+} ion.

The experimental set-up is shown in Figure 1. The Eu^{3+} ion has a charge-transfer band in the region of 200–300 nm.⁴ The photoreduction of $\text{Eu}^{3+}(\text{TODGA})_n$ was performed by irradiation of the fourth harmonic (266 nm, 50 mJ/cm²) of Nd:YAG laser (Continuum, Surelite II) into the 1-octanol solution. To detect the reduced Eu^{2+} ion by LIF spectroscopy, the liquid–liquid extraction system was irradiated with the third harmonic (355 nm, 2 mJ/cm²) of Nd:YAG laser (Spectra Physics, INDI-40) from the opposite side of the reduction laser. The pulse width and repetition rate of the Nd:YAG lasers were ≈ 20 ns and 10 Hz, respectively. The fluorescence from the Eu^{2+} ion excited by the 355-nm laser was observed from the side of the cell by an optical fiber coupled with a biconvex lens, and was introduced into a monochromator (SPEX 270M). The lifetime of the fluorescence from Eu^{2+} is short (≈ 160 ns), even though the Eu^{2+} ions are stabilized by 15C5.⁵ To observe the short-lifetime phenomenon with high signal to noise ratio, we detected the fluorescence in 50–1000 ns duration after the 355-nm laser pulse by using optical gating. By moving up and down simultaneously the excitation light and the detection system, we detected the LIF signals from Eu^{2+} in the 1-octanol solution, the water and the interface maintaining the relative positions between the reduction and excitation lights.

Figures 2a and 2b show the fluorescence spectra excited by the 355-nm laser in the 1-octanol solution and the water. As shown in Figure 2a, a broad emission band peaking at 430 nm appeared in the LIF spectrum taken at 20 min after the start of the reduction-laser irradiation. This band intensity decreases

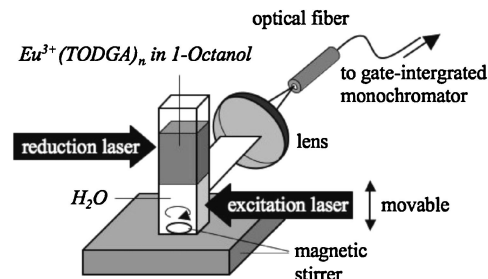


Figure 1. Experimental set-up for photoreduction and LIF spectroscopy.

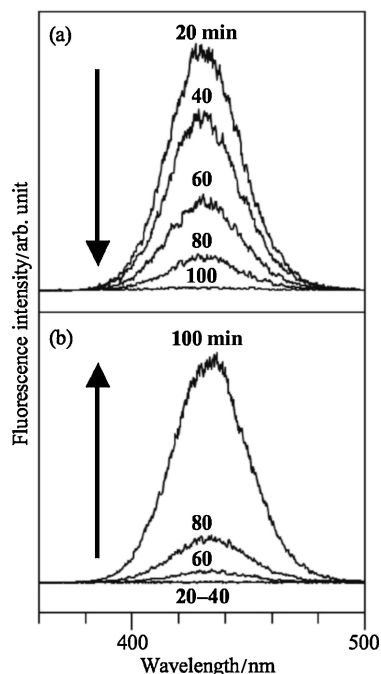


Figure 2. Fluorescence spectrum (a) in 1-octanol and (b) in water.

with increase in irradiation time. On the other hand, as shown in Figure 2b, the fluorescence in water is absent during ≈ 60 min after the start of the photoreduction, and then the intensity suddenly increases with increasing irradiation time. Both bands in Figures 2a and 2b are assigned to the fluorescence from the complex of Eu^{2+} and 15C5, because the bands were unobserved in the absence of 15C5 and because the Eu^{3+} ion and its complexes have little absorbance at 355 nm. From the fact that the periphery of Eu^{2+} can be covered by three 15C5 molecules,⁵ the similarity of the wavelength and shape of the bands between Figures 2a and 2b is attributed to the weak interaction between Eu^{2+} and solvents, which arises from full occupation of the first coordination sphere of Eu^{2+} by 15C5. The $\text{Eu}^{2+}(\text{15C5})_m$ complex observed in the water should come from the 1-octanol solution, because the photoreduction of Eu^{3+} was performed only in the 1-octanol solution. Therefore, it is obvious that the back extraction from the 1-octanol solution to the water is induced in this liquid–liquid extraction system by the ion reduction using the 266-nm laser.

To obtain information on the back-extraction mechanism, we observed the LIF spectra of $\text{Eu}^{2+}(\text{15C5})_m$ at 5-min intervals in the 1-octanol solution, water, and the interface. Figures 3a–3c show dependence of the fluorescence intensity of $\text{Eu}^{2+}(\text{15C5})_m$ on the irradiation time at the respective positions. Figure 3a shows that the fluorescence intensity of $\text{Eu}^{2+}(\text{15C5})_m$ in the 1-octanol solution increases within 1 min after the start of the photoreduction, stays at maximum for ≈ 20 min, and then gradually decreases after 20 min. The fluorescence intensities have similar temporal evolution between Figures 3b and 3c. The fluorescence from $\text{Eu}^{2+}(\text{15C5})_m$ is negligibly small for ≈ 60 min after the start of the photoreduction and then increases exponentially after 60-min irradiation both at the interface and in water. Considering the instability of Eu^{2+} in solution,⁶ we interpret the dependence of the fluorescence intensity on the irradiation time in Figures 3a–3c as follows: first, the Eu^{2+} ion, produced by the

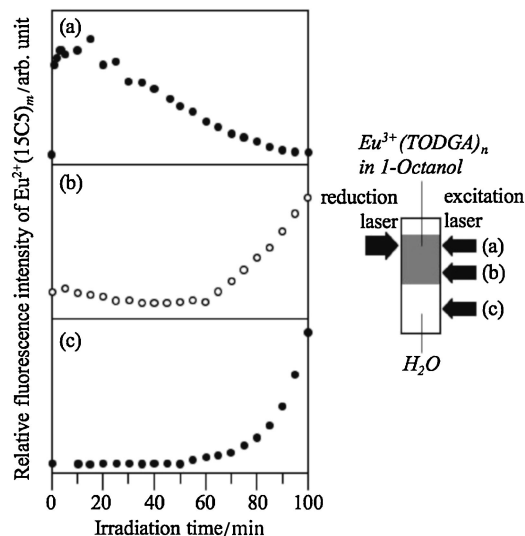


Figure 3. Dependence of fluorescence intensity of $\text{Eu}^{2+}(\text{15C5})_m$ on irradiation time (a) in 1-octanol, (b) at interface and (c) in water.

photoreduction and ligand disengagement of $\text{Eu}^{3+}(\text{TODGA})_n$, is rapidly chelated and stabilized by 15C5. Then, the $\text{Eu}^{2+}(\text{15C5})_m$ complex slowly diffuses in the 1-octanol solution being repeatedly oxidized and reduced. Finally, after 60 min the $\text{Eu}^{2+}(\text{15C5})_m$ complex around the interface is immediately extracted to the water. Based on viscosity of 1-octanol ($\eta = 8.93$ mPa·s) and the water ($\eta = 1.00$ mPa·s), the diffusion coefficient of $\text{Eu}^{2+}(\text{15C5})_m$ in 1-octanol, which is proportional to reciprocal of the viscosity, is assumed to be much smaller than that in the water. It may contribute to the slow diffusion of $\text{Eu}^{2+}(\text{15C5})_m$ in 1-octanol and the immediate extraction to the water at the interface.

In summary, we have studied back-extraction using photoreduction by the fourth harmonic of Nd:YAG laser in a liquid–liquid system composed of 1-octanol containing $\text{Eu}^{3+}(\text{TODGA})_n$ and water. We investigated the behavior of reduced Eu^{2+} ion by LIF spectroscopy in a 1-octanol solution, in water and at the interface, and concluded that (i) the Eu^{2+} ion is chelated and stabilized by 15C5 immediately after photoreduction, (ii) the diffusion of $\text{Eu}^{2+}(\text{15C5})_m$ in 1-octanol is slow, and (iii) the transfer of $\text{Eu}^{2+}(\text{15C5})_m$ from the interface to the water quickly occurs.

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