Dynamic Microscopic Extraction of Europium(III) with 2-Thenoyltrifluoroacetone Observed as Random Fluorescence Flashes at Dodecane–Water Interface

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Many random circular flashes of Eu(III) fluorescence (8–23 μm in diameter) appeared at the interface in the extraction of Eu(III) with 2-thenoyltrifluoroacetone (Htta) into dodecane, when a Eu^{3+} aqueous solution was added after pre-distribution of Htta in the aqueous phase. The flash was caused by the interfacial reaction between a pre-generated micro-aggregate of $Eu(tta)^{2+}$ in the aqueous phase and excess Htta in the dodecane phase. The interfacial reaction produced more fluorescent $Eu(tta)_3$, which diffused away into the dodecane phase.

The role of liquid–liquid interface in solvent extraction systems is now investigated extensively, because it has specific functions in the adsorption of ligand and the kinetics of metal complexation at the interface. Various spectroscopic methods have been developed for direct measurements of species at the liquid–liquid interface.[1] In recent years, not only physical properties and structures of the interface but also transfer processes through the interface have been discussed. The interfacial concentration of adsorbed species is commonly assumed to be two-dimensionally homogeneous, but our direct microscopic observation for the liquid–liquid interface found an inhomogeneous interfacial layer of Pd(II)–porphyrin complexes for the first time.[2] There have been no reports on the microscopic observation or measurement of extraction processes occurring at the liquid–liquid interface.

Europium(III) is frequently used as a fluorescent probe,[3] since the fluorescence intensity and lifetime are significantly affected by the microenvironment around the Eu(III). Eu^{3+} in aqueous solutions is hard to be excited because of the much lower molar absorption coefficient (about $1\,M^{-1}\,cm^{-1}$) ($1\,M = 1\,mol\,dm^{-3}$). Eu(III) bound to an appropriate organic ligand shows a drastically enhanced fluorescence. Some ligands are easily excited owing to its high absorption coefficient, followed by an intramolecular energy transfer to Eu(III). Since a water molecule directly bound to Eu(III) is a typical quencher for the Eu(III) fluorescence,[4] the fluorescence lifetime (τ_f) enables us to calculate the number of the water molecules, leading to the estimation of chemical species.[3,4]

For the enhancement of Eu(III) fluorescence, 2-thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, Htta) has been used because its higher molar absorption coefficient (about $10^4\,M^{-1}\,cm^{-1}$), a high efficiency of energy transfer to Eu(III), and a high stability constant. Htta has also been known to be a common extractant for lanthanoids.

Dodecane (extra pure grade, Nacalai) was used after purification by passing through a silica gel column. Water was purified with a Milli-Q system (Milli-Q SP. TOC., Millipore). Htta (Dojindo Lab.) was dissolved in dodecane in a concentration range of 2.1×10^{-5}–$2.1 \times 10^{-3}\,M$, and the solution was used as the organic phase. An aqueous stock solution of Eu^{3+} was prepared by dissolving europium oxide (Eu_2O_3, Wako) in diluted perchloric acid. HEPES (2-[4-(2-hydroxy-ethyl)-1-piperazinyl]-ethanesulfonic acid) was used as a buffer.

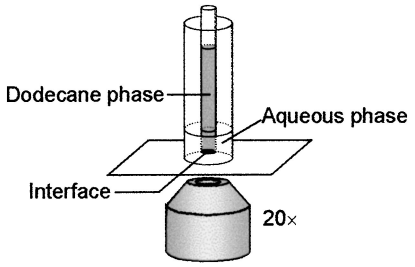

Figure 1. Schematic drawing of the microscopic observation system of Eu(III) extraction with Htta in the dodecane–water interfacial region.

The microscopic observation system is illustrated in Figure 1 schematically. An inverted microscope (TMD300, Nikon) with a microscope objective (Plan Fluor 20×, NA 0.50) was employed. A fluorescence filter block consisted of a 330–385 nm excitation filter, a 400 nm dichroic mirror, and a 580–900 nm emission filter. The filters allowed us to detect only Eu(III)-tta complexes. Excitation light from a light source irradiated the interface through the objective, and the fluorescence was collected with the same objective and then introduced to a detector. A glass tube (5.0-mm o.d., 3.3-mm i.d., 20-mm height) was attached onto a coverslip. A 20-mm^3 aqueous buffer solution was put into the glass tube. A glass capillary (0.94-mm o.d., 0.46-mm i.d., 32-mm height) was set to a manipulator (ONM-1, Olympus). About 4-mm^3 dodecane solution of Htta was introduced into the capillary, and then the capillary was inserted quietly into the aqueous phase in the glass tube. After about 2 min, a 20 mm^3 of Eu^{3+} aqueous solution was added into the glass tube and the aqueous solution was stirred gently by a small looped platinum wire for some time. The final concentrations of Eu^{3+} and $NaClO_4$ were $1.0 \times 10^{-5}\,M$ and 0.1 M, respectively, and the final pH was 6.6–6.9. The horizontal position of the interface almost agreed with that of the bottom edge of the capillary, which allowed us to focus the interface easily. The small interfacial area (0.17 mm^2) gave nonfluctuated interface. The fluorescence image of the interface was observed with a 100-W Hg lamp and a CCD camera (KP-201, Hitachi) as a light source and a detector, respectively. Time-resolved fluorescence measurements were done with a N_2 laser (LN120, Laser Photonics; 337 nm, pulse width 300 ps, power 70 $\mu J\,pulse^{-1}$) and a streakscope (C4334, Hamamatsu Photonics) in a similar optical system to the previous paper.[5] All the experiments were carried out in a thermostated room at 25 °C.

The extraction constant (K_{ex}) for the Eu^{3+}–Htta–dodecane

system has not been reported so far, but the value is available in the cyclohexane system as 4.07×10^{-8}. Some batch experiments indicated that almost all of the Eu^{3+} was extracted into the dodecane phase at the initial concentration of Htta ($[Htta]_{init}$) higher than 1.0×10^{-3} M at pH 6.6–6.9. This fact was also supported by the estimation with the K_{ex} value.

When $[Htta]_{init}$ was higher than 1.2×10^{-3} M, many circular fluorescence flashes were observed at the dodecane–water interface at random. Figure 2 shows typical examples of the fluorescence images at the dodecane–water interface. Flashes were not observed at the beginning, but it began to flash after about 3 min. When the focal plane was adjusted into the dodecane or aqueous phase, no flashes or particles were observed, indicating that this phenomenon occurred only at the dodecane–water interface. Also, fluorescent solid domains of various sizes were accumulated at the interface as shown in Figure 2, independent of the flashes. Fluorescence spectra and the observed τ_f values of the interface suggested the existence of $Eu(tta)_3$ and some aggregates at and near the interface.[3,4]

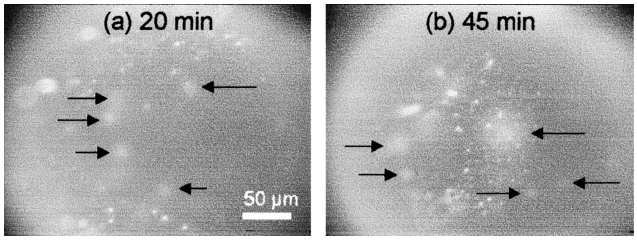

Figure 2. Fluorescence images at the dodecane–water interface at 20 min and 45 min after the addition of the Eu^{3+} aqueous solution. Blurred circular white images indicated by arrows were the fluorescence flashes, and clear white images of various sizes were interfacial fluorescent solid domains. Htta, 2.1×10^{-3} M; Eu^{3+}, 1.0×10^{-5} M; pH, 6.6.

An instance of a time profile for a single fluorescence flash is shown in Figure 3. The flash appeared quickly and disappeared slowly, and its area was spread out. The flash center was brightest at the beginning (0 s), and the intensity decreased gradually. These results suggested that no or weak fluorescent aggregates of Eu(III) were generated in the aqueous phase, they occasionally reached to the interface and a more fluorescent $Eu(tta)_3$ was produced with Htta at the interface. The diffusion of $Eu(tta)_3$ into the dodecane phase caused the fading of the flash. The time profile of other flashes was similar.

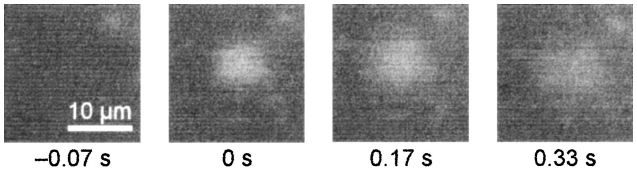

Figure 3. Continuous images for a single fluorescence flash at 53 min. The experimental condition was the same as that in Figure 2.

The average size of the flashes was about 8 μm in diameter at 3 min, and then the size increased to 23 μm with the elapse of time. After 90 min, the size occasionally reached to about 70 μm. The number of flashes observed for 30 s in an interfacial area of 230×310 μm was 30 counts at the beginning, and then it increased with time. It reached to 160 counts after 15 min.

When the Eu^{3+} solution was added before inserting the capillary including the organic phase, no fluorescence flashes were observed. This fact meant that Htta distributed into the aqueous phase within 2 min played a key role in this curious phenomenon. The distribution constant (K_D) of Htta in the dodecane–water system[6] and the acid-dissociation constant (pK_a) of Htta were 3.19 and 6.23, respectively. Because of the smaller volume ratio of the organic to aqueous phases ($0.1 = 4\,mm^3/40\,mm^3$), 91–95% of initial amount of Htta in the dodecane phase should be distributed into the aqueous phase at pH 6.6–6.9 at equilibrium.

An aliquot ($5\,cm^3$) of the dodecane solution of 2.1×10^{-3} M Htta was shaken with an equal volume of an aqueous buffer solution (pH 7.0) in a test tube for 30 min. A part of the aqueous phase was taken out and an aliquot of a Eu^{3+} solution was added. The final Eu^{3+} concentration and pH were 1.0×10^{-5} M and 6.6–6.9, respectively. Within 3 min, the aqueous solution showed a definite fluorescence of Eu(III) with 369 nm excitation light and its τ_f value was 149 μs, indicating $Eu(tta)^{2+}$.[4] Also, some micro-aggregates emitting weak fluorescence were observed with the fluorescence microscope. These facts suggested the possibility of the pre-generation of $Eu(tta)^{2+}$ aggregates with ClO_4^- as a noncharged species, $[Eu(tta)^{2+}]_m(ClO_4^-)_{2m}$, in the aqueous phase in the microscopic observation system.

Figure 4 shows the scheme of flash generation of $Eu(tta)_3$ at the interface. The aggregates were hard to be detected in the aqueous phase owing to their much weak fluorescence and the large background of the fluorescent interface. The increment of the flash size with time means an increase in the aggregate size.

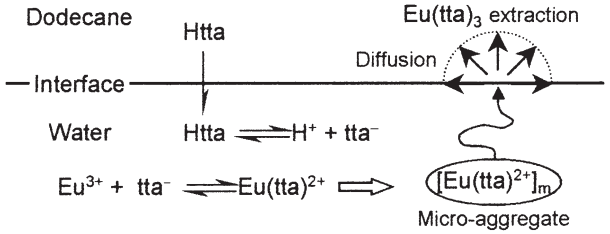

Figure 4. Overall scheme for the micro-aggregate extraction of Eu^{3+} with Htta in the dodecane–water interfacial region.

When toluene was used instead of dodecane, no fluorescence flashes appeared at the toluene–water interface at the same Eu^{3+} and Htta concentrations. Since K_D was 39.8 in this system,[7] which was much larger than the dodecane system, an enough amount of Htta would not be distributed into the aqueous phase before the addition of the Eu^{3+} solution.

In conclusion, the present study shows that a microscopic heterogeneous extraction occurs at the liquid–liquid interface even in the commonest extraction system for the first time.

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