Measurements of Interfacial Complexation of Samarium(III) and its Fluorescence Lifetime by Micro-two-phase Sheath Flow/Fluorescence Microscopy

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The micro-two-phase sheath flow/fluorescence microscopy was used for the fluorescence lifetime measurement for the first time. An inner micro-flow of the toluene solution of samarium(III) complex was flowed in an aqueous phase stream. From the fluorescence decay images observed in the inner flow just after the excitation point, the fluorescence lifetime of the complex was observed. By flowing a toluene solution of ligands into the Sm(III) aqueous stream, the interfacial formation of the fluorescent complex was observed.

Studies on chemical reactions and transfer phenomena in micro-liquid/liquid systems have attracted much attention in various research fields concerning liquid/liquid or membrane/liquid systems. Recent studies have reported that the interfacial reaction plays important roles in the kinetic mechanisms of two-phase reactions, especially in the kinetics of the solvent extraction of metal ions.[1] It is indispensable to measure the rate of the interfacial reaction for elucidating the extraction mechanism. We have recently reported a novel method named two-phase sheath flow method, which enabled us to measure a fast interfacial complexation rate within a few milliseconds in 1-butanol/water system.[2] In this paper, toluene was used as an inert organic solvent. When the toluene solution was made to flow from a capillary tip at a high flow rate into an aqueous solution flow, it was possible to observe a fresh interface within less than 0.1 ms. Therefore, this method was expected to measure a fast diffusion dynamics in the interfacial nano-region and to detect a short-lived intermediate in the sequential complex formation.

The ternary complex composed of samarium(III), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta), and tri-*n*-octylphosphine oxide (topo) was chosen in the present study. The relatively long fluorescence lifetime of the complex is advantageous to identify the species from the lifetime in the present method. At first, the fluorescence lifetime was measured from the fluorescence decay profile of the complex along the inner organic phase flow, in order to demonstrate the utility of this method as a new lifetime measurement technique. Then, the present method was applied to measure the complex formation at the interface in the Sm(III) extraction system.

All reagents used in this study were of analytical grade and used without further purification. Aqueous solutions of samarium(III) chloride contained 1.0×10^{-3} mol dm^{-3} 2-morpholinoethanesulfonic acid (MES) as a buffer, and pH was maintained at 6.0 ± 0.1. All aqueous solutions were prepared with water purified by the Milli-Q system (Gradient A10, Millipore). All measurements were carried out in a thermostated room at 296 ± 1 K.

Ten cubic centimeter of 1.1×10^{-3} mol dm^{-3} Htta and 1.1×10^{-3} mol dm^{-3} topo toluene solution and the same volume of 1.1×10^{-3} mol dm^{-3} Sm(III) aqueous solution (pH 6.0) containing 1.2×10^{-2} mol dm^{-3} sodium chloride were shaken for 2 h. After phase separation, the fluorescence spectra and lifetime of the extracted Sm(III) complex were measured with a pulse-excited fluorescence spectrometer (LS50B, Perkin Elmer). The wavelength for excitation was set at 390 nm. The specific fluorescence peaks of Sm(III) complex were observed in the wavelength range of 550–750 nm. The fluorescence lifetime of the complex in toluene phase was obtained as 83 μs. In this extraction condition, the extracted species was thought to be $Sm(tta)_3(topo)_2$,[3] though some other types of extractable species were reported in the synergistic extraction of Sm(III) in the other conditions.[4]

The two-phase micro-flow system was made by the same way as reported previously.[2] The organic phase solution was made to flow by a high pressure syringe pump (SSC-3700, Senshu Scientific). The second-harmonic light of a mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics), of which wavelength and power were 390 nm and 60 mW, respectively, irradiated through a microscope objective (20×, NA 0.75) of the inverted microscope (TE300, Nikon) and an excitation micro-spot was formed on the organic flow. The emitted fluorescence was corrected by the same objective and observed by an intensified CCD camera (PentaMAX, Princeton Instruments) after the reduction of undesirable light by a barrier filter. The spectra of emitted fluorescence were measured with a streak scope (C4334, Hamamatsu Photonics).

Figures 1a and 1b are CCD camera images of the flow system with and without illumination, respectively. In this flow system, pure water was used as the outer flow. The flow rates of the organic and aqueous phases were 30.0 mm^{3}min^{-1} and 1.00 cm^{3}min^{-1}, respectively. The linear velocities of the inner and outer flows were estimated as about 2–5 m s^{-1} and 0.3 m s^{-1}, respectively. When the organic solution containing the extracted Sm(III) complex was flowed as the inner flow, the tailing of the fluorescence was appeared like a "comet" along the flow. This means that the Sm(III) complex, excited by the laser irradiation at a fixed position, emitted fluorescence downstream, since Sm(III) complex had a long fluorescence

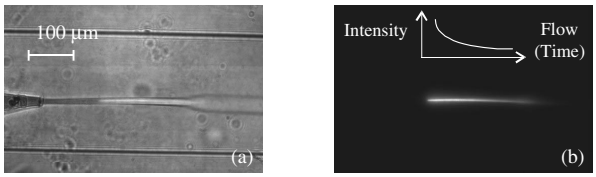

Figure 1. CCD camera images of the toluene/water micro-flow system with illumination (a) and without illumination (b). The organic flow cylinder was of 310 μm length, and broke to form droplets downstream continuously. The tailing of the fluorescence is shown along the organic phase flow.

lifetime. The continuous cylindrical inner flow was broken to droplets at the downstream as shown in Figure 1a.

It is clear in Figure 1a that the diameter of the inner flow slightly increases along the flow direction. This is due to the situation that the linear velocity of the aqueous phase flow was slower than that of the inner flow and then the linear velocity of the inner flow was decreased by the frictional force against the aqueous phase. Therefore, the linear velocity of the inner organic phase flow was corrected by considering the shape of the organic flow measured from the CCD images. In addition, the linear velocity at the interfacial region of the organic phase flow might be further reduced by the friction with the aqueous phase.

A toluene solution of the Sm(III) complex, prepared by an extraction, was used as the inner flow and the different positions of the inner flow were irradiated by the excitation light along the flow line. The fluorescence decay profile was obtained at each excitation position as shown in Figure 2a, in which the distance between the excitation position and the capillary tip was set 5.4, 84, and 154 μm. The corresponding contact times of the two phases were calculated as 0.5, 15, and 40 μs, respectively. The fluorescence spectrum measured in this flow system with the streak scope was identical to that measured by a pulse-excited fluorescence spectrometer. As noted in Figure 2a, the fluorescence intensity had a maximum at the excited position and it decreased gradually along the flow direction. However, the intensities increased a little at the contact time of about 70–80 μs in all cases. This time corresponded to the position where the continuous flow was collapsed, as seen in Figure 1a. It appeared that the fluorescence intensity at the excitation point increased with the increase in the contact time. This was due to the increase in the volume excited by the laser irradiation, since the diameter of the inner flow increased with the contact time. The fluorescence decay profile excited at the position of 5.4 μm was different from others, showing the gradual increase after the excitation. The cause of this result is that the flow was bent near the capillary outlet and was not entirely on the focal plane of the microscope. From the fitting of each fluorescence decay curve in Figure 2a to a single exponential function, the fluorescence lifetime was calculated as 85 ± 13 μs as an averaged value. This value coincides well with 83 μs measured in toluene with the pulse-excited fluorescence spectrometer. This result clearly demonstrated that this microflow technique could be applied to the measurement of the fluorescence lifetime in the range of submillisecond.

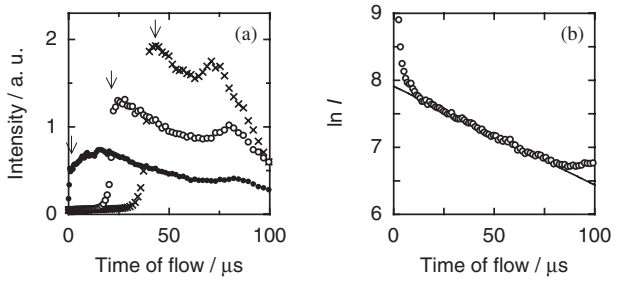

Figure 2. (a) The fluorescence decay profiles measured at the different excitation positions of the inner flow as indicated by arrows; 0.5 (●), 15 (◯), and 40 μs (×). (b) The fluorescence decay profiles of the Sm(III) complex formed at the toluene/water interface after the contact time of 65 μs.

The complexation of Sm(III) with Htta and topo in toluene/water system was investigated with this technique. The aqueous phase (pH 6.0) contained 1.1×10^{-2} mol dm^{-3} Sm(III), and the organic phase was a toluene solution of 5.2×10^{-3} mol dm^{-3} Htta and 6.2×10^{-3} mol dm^{-3} topo. By moving the microscope objective perpendicular to the flow, the focal point could be shifted from the flow center to the interface and the interfacial region could be excited selectively. The intensity of the interfacial region was higher than that of the flow center. This means that the complexation of Sm(III) has been taken place in the interfacial region. Figure 2b shows the fluorescence decay profile, irradiated at 280 μm downstream from the capillary outlet, and the reaction time was calculated as 65 μs in this flow system. The fast decay component in this figure was ascribable to the emission from the bulk organic phase, which was not eliminated by the filters. The lifetime obtained from this decay curve was 69 μs. This was shorter than the fluorescence lifetime 85 μs for $Sm(tta)_3(topo)_2$ complex extracted into the toluene under the conditions described above. It is known that the fluorescence lifetime of some lanthanide(III) complexes depends on the number of the coordinated water molecules.[5,6] As for the Sm(III) complexes, any definite relation between the lifetime and the water molecules has not been reported, but we observed that the lifetime of Sm(III)-tta complex in the absence of topo was very short and that the addition of topo significantly increased the lifetime. Therefore, it was suggested that the detected fluorescent Sm(III) species contained both tta and topo complexes, and it might still have some hydrated water molecules. It was also probable that the complex detected at the interface was one of the intermediates in the sequential complexation, not the extracted species. More detailed study is required for the identification of the formed species at the interface.

The present study demonstrated that the micro-two-phase sheath flow/fluorescence microscopy was useful for the measurement of lifetime of the Sm(III) complex extracted with Htta and topo in toluene phase. It was also demonstrated that the present technique could detect the interfacial complexation of the rare earth ion with the ligands in toluene phase. This flow method is promising to detect a short-lived intermediate in the sequential interfacial complexation, which gives a new insight into the interfacial reaction mechanism.

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