A LIQUID/LIQUID OPTICAL WAVEGUIDE WITH MISCIBLE SOLVENTS TO OBSERVE COMPLEXATION REACTION

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ABSTRACT

A liquid-core/liquid-cladding optical waveguide using a miscible solvent system, i.e., 50 % ethanol for the core and water for the cladding, was applied to observe the complexation reaction of aluminum ion (Al^{3+}) and lumogallion. The complexation reaction was monitored by measuring the fluorescence of Al^{3+}- lumogallion complex (ex. 473 nm, em. 565 nm). The reaction started at the interface between the core and clad solutions, then, the region of the reaction gradually expand to the center of the core solution. This result was compared with that of computational fluid dynamics (CFD) simulation of the LLW, those showing the consistent result with each other.

KEYWORDS

Liquid-core/liquid-cladding optical waveguide, complexation reaction, aluminum ion, lumogallion, computational fluid dynamics.

INTRODUCTION

The concept of a liquid/liquid optical waveguide (LLW), which has a liquid-core/liquid-cladding structure, has firstly been introduced by us [1, 2], then, it has been extended to micro-fluidic microchips by some other research groups, where its potentialities as an optical switch, an evanescent coupler and so on have intensively been investigated, and consequently the field of "optofluidics" has been being developed rapidly [3-5]. Our purpose, on the other hand, has been to apply the LLWs for reaction cells to study liquid/liquid interfacial phenomena. Our LLWs have been fabricated using the sheath flow from a concentric stainless capillary (core) and an outer glass capillary (clad). Miscible solvent-systems such as tetrahydrofuran (THF) /water, 50 % ethanol/water, 15 % NaCl aqueous solution/ water and etc. have been used to form the LLWs. In particular, the THF/water LLW was applied to observe the ion-pair solvent extraction process of 1-anilino-8-naphthalene sulfonate (ANS) and hexadecyltrimethylammmonium ion (CTA) [2].

In this work, a 50 % ethanol/water LLW was applied to observe the complexation reaction of aluminum ion (Al^{3+}) and lumogallion by measuring the fluorescence of Al^{3+}-lumogallion complex. Moreover, the result was compared with that of computational fluid dynamics (CFD) simulation of the LLW.

EXPERIMENT

Lumogallion (4-chloro-6-(2,4-dihydroxyphenylazo)-1-phenol-2-sulfonic acid), which is a famous fluorometric reagent for Al^{3+}, was purchased from Tokyo Chemical Co. Ltd, Japan and was used without further purification. The experimental set up of the LLW system is shown in Figure 1. The 50% ethanol solution containing 0 to 40 μmol/dm^3 Al^{3+} (the core solution) and the aqueous solution containing 200 μmol/dm^3 lumogallion (the clad solution) were sent into the inner capillary and the outer capillary, respectively, with a gravity-driven method. The inner capillary was a stainless capillary; i.d., 0.13 mm; o.d., 0.31 mm; the tip of the capillary was tapered. The outer capillary was a square glass capillary; i.d., 1.2 x 1.2 mm; o.d., 1.7 x 1.7 mm; length, 200 mm. The source light, a blue laser (473 nm), was introduced into the inner flow through an optical fiber (o.d., 70 μm; N.A., 0.2). The Al^{3+}-lumogallion complexation reaction was monitored measuring the fluorescence of Al^{3+}-lumogallion complex (λ_{max}, 565 nm) with a microscope system (a custom-made system, Olympus Co. Ltd., Japan) having a CCD camera (Ratiga 2000R, QImaging Co. Ltd., Canada) or a multi-channel CCD detector (PMA-11, Hamamatsu Photonics Co. Ltd.,). The microscope system was moved manually along with the long axis of the LLW. CFD simulation was performed using a commercial CFD software, STAR-CD.

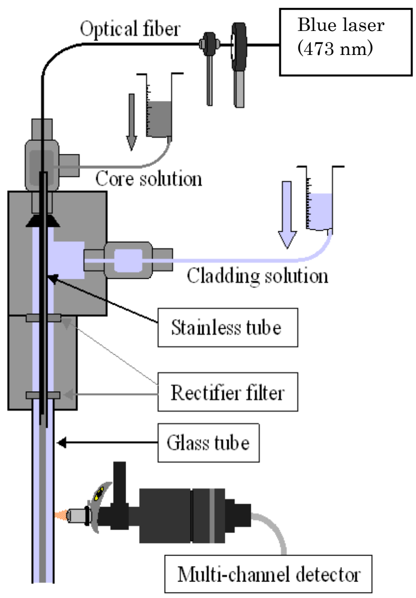

Figure 1. Schematic diagram of LLW system

RESULTS AND DISCUSSION

The 50 % ethanol/water LLW was stable up to at least 150 mm from the tip of the inner-capillary in the range of 1.4 to 2.3 cm s^{-1} of the average linear velocity of both flows, where almost no leakage of the guided light was observed.

The fluorescence signal intensity of Al^{3+}-lumogallion increased along with the increase in the distance from the tip of the inner-capillary, i.e., the increase in the contact time of the core solution and the clad solution, as shown in Figure 2. Moreover, the interference effect of citric acid with this reaction is also shown in the same figure. Al^{3+} and citric acid are known to form a stable complex, thus, the addition of citric acid to the core solution prevented Al^{3+} from the formation of Al^{3+}-lumogallion complex. Similar effect was also observed when oxalic acid was added to the core solution. These results may show that aquo-Al^{3+} ion and the complexed Al were distinguished from each other in this measurement, that suggesting the potentiality of this LLW system as a new tool for elemental speciation analysis for Al. Moreover, Figure 3 shows the photos of the fluorescence signals from the LLW. These figures shows that the reaction started at the interface between the core and the clad solutions, then, the region of the reaction gradually expanded to the center of the core solution as shown in the same figures.

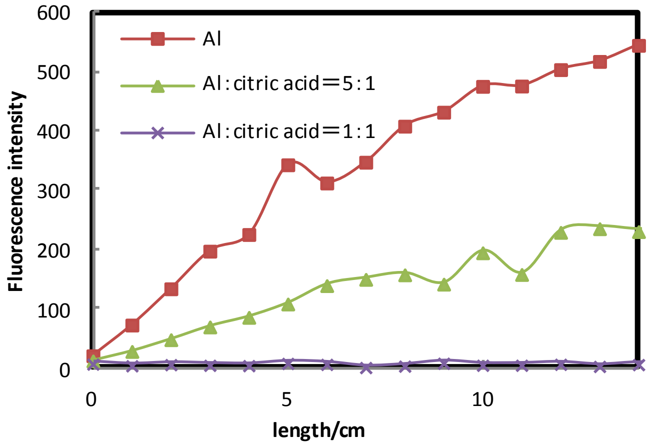

Figure 2. Fluorecence signal intensity of Al^{3+}-lumogallion complex along with the distance from the tip of the inner capillary
Conditions: Core solution, Al^{3+} 40μM (+citric acid) in 50% EtOH solution; Clad, Lumogallion 200 μM in pH6.2 Buffer: Linear Velocities of Core and Clad, 14 cm/s, 1.4 cm/s, respectively

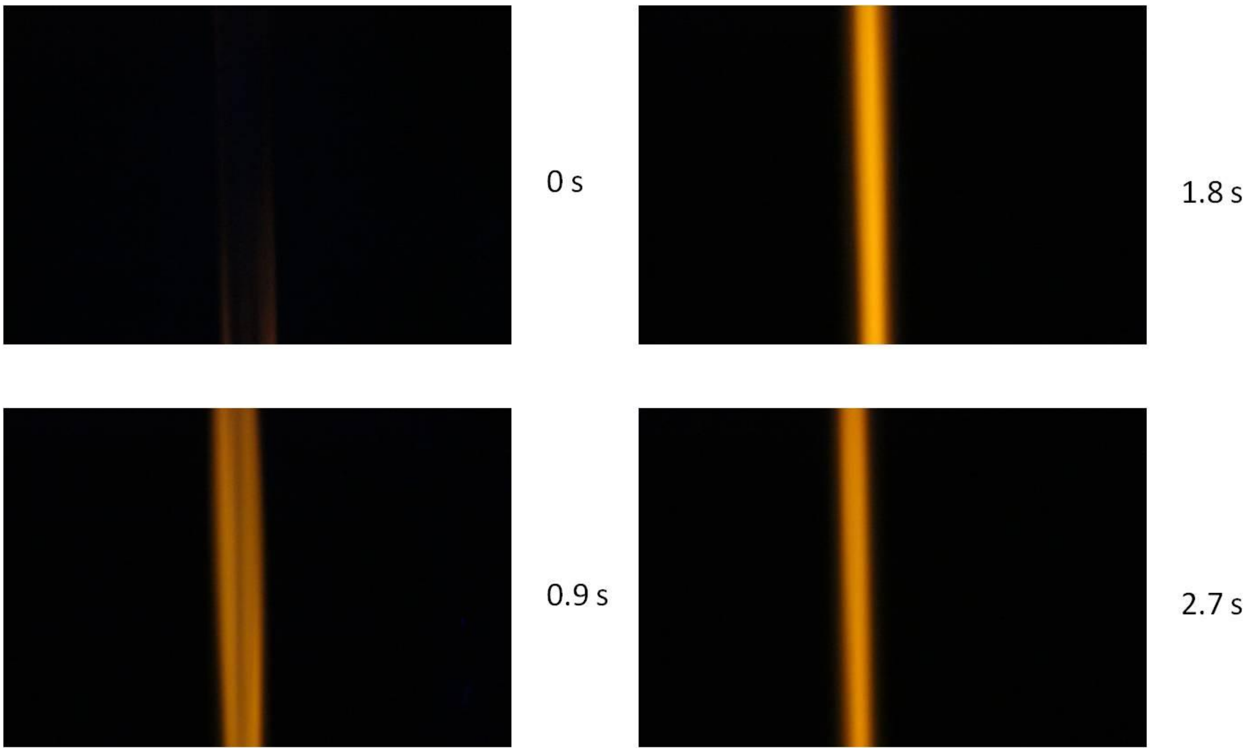

Figure 3. Photos of the fluorescence from LLW.
0 to 2.7 s show the contact time of the core solution and the clad solution (the distance from the tip of inner capillary)
Ratio of Linear Velocities of Core and Clad before Merging, 1.0 : 1.0
Average Linear Velocity, 2.24 cm/s

Then, the CFD simulation of Al^{3+} and lumogallion was performed. The results on a) Al^{3+} concentration and b) lumogallion concentration are shown in Figure 4, respectively. The conditions of the simulations are also summarized in the same figure. Moreover, the products of a) Al^{3+} concentrations and b) lumogallion concentrations in Figure 4 are shown in Figure 5, which should be a first approximation to the concentration of Al^{3+}-lumogallion complex. As shown in Figure 5, the CFD simulation predict that the fluorescence starts at the interface at 0 s; the peaks of the fluorescence move toward the center of the core at 0.9 s; the whole core emits the fluorescence after 1.8 s. These results are in good agreement with those of the experiment (see Figure 3), that confirming the usefulness of the CFD simulation.

Conclusively, the LLW was able to be applied to observe the complexation reaction of Al^{3+} and lumogallion. Moreover, the CFD simulation was effective to understand the behavior of the molecules in the LLW.

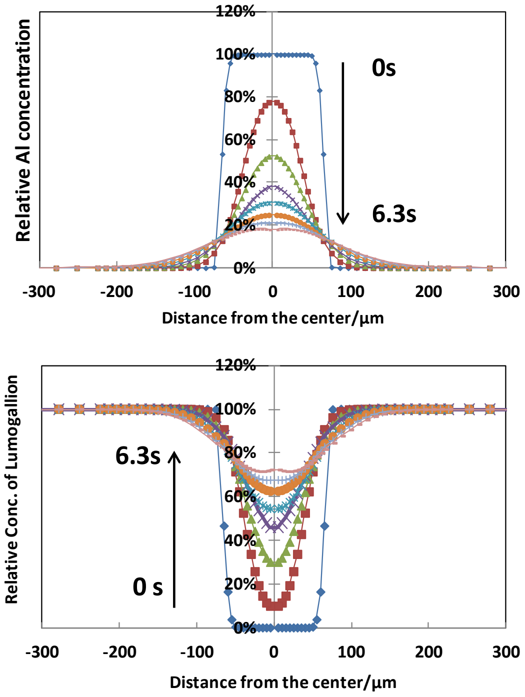

Figure 4. CFD simulation of a) Al^{3+} concentration and b) lumogallion concentration.

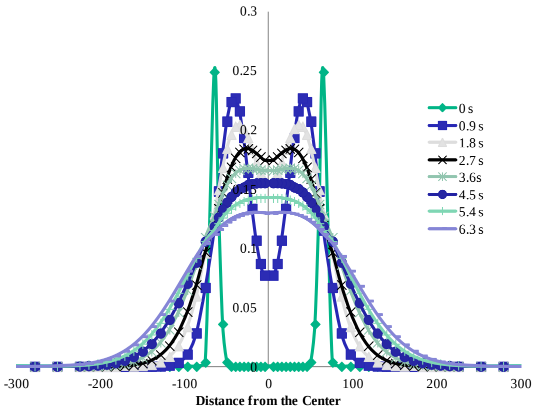

Figure 5. CFD simulation of the product of a) Al^{3+} concentration and b) lumogallion concentration in Figure5.

The conditions of the simulation:
Core solution: Al 40 μM
Clad solution: Lumogallion 200 μM
Linear Velocity Ratio of Core and Clad: 0.76 : 1
Average Linear Velocity: 2.24 cm/s
Program : STAR-CD
Diffusion Coefficient of Al^{3+}: 5.94×10^{-10} $m^2 s^{-1}$
(Value of Cr^{3+})
Diffusion Coefficient of Lumogallion: 2.8×10^{-10} $m^2 s^{-1}$
(Value of Rhodamin-6G)

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