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Measurement of local chemical reaction rate in a microchannel by using luminol chemiluminescence

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ABSTRACT

The present paper reports local mixing and chemical reaction in a T-junction microchannel investigated using luminol chemiluminescence (CL). Generally, the degree of mixing in a microchannel is calculated based on the deviation of the obtained concentration profiles from the uniform concentration using a fluorescence technique. In the present study, the luminol CL reaction is applied to estimate the local chemical reaction rate at the interface between two liquids in the microchannel. Luminol emits blue chemiluminescence when it reacts with hydrogen peroxide at the mixing layer. Experiments were carried out using a T-junction microchannel 200 μm in width and 50 μm in depth that was cast in a PDMS chip. The chemiluminescence intensity profiles clearly show the mixing layer at the interface between the two liquids. The experimental results are compared with the results of a numerical simulation that involves solving mass transport equations that include a chemical reaction term. By calibrating the CL intensity to the chemical reaction rate estimated by the numerical simulation, the local chemical reaction profile can be quantitatively estimated from the CL intensity profile. The effects of the chemical species concentrations on the local mixing and the chemical reaction were investigated.

1. Introduction

Chemical reactions in micro-fluidic devices are strongly affected by mixing performance. Mixing in a microchannel flow occurs primarily by means of molecular diffusion at the interface between two liquids due to laminar flow at a low Reynolds number. The diffusion time τ_d for mixing over the channel width d is proportional to the square of the channel width, i.e., $\tau_d \propto d^2$ [1]. Thus, mixing in the microchannel has an advantage in that the diffusion time is decreased significantly. However, when the channel width is approximately 100 μm, molecular diffusion can mix two liquids streams within several seconds. Solutions used in biological and chemical analyses contain large molecules, such as globular proteins, the diffusion coefficients of which are one or two orders of magnitude lower than the diffusion coefficients of the two liquids [1]. In homogeneous mixing, the micro-fluid device requires a relatively long microchannel.

The chemical reaction in the microchannel is related to both time scales, namely, the mixing time for diffusion and the time required for the chemical reaction [2]. When these time scales are comparable, the local chemical reaction in the microchannel depends on local diffusion and the mixing process in the mixing layer. These processes are elementary phenomena related to the reaction diffusion system [3], but are important for estimating and controlling the performance of the micro-fluidic device. However, local mixing and chemical reaction rates in the microchannel are difficult to estimate experimentally. Therefore, analysis of local mixing and chemical reaction rates will contribute to the development of micro-fluidic devices.

Mixing in a microchannel has generally been estimated based on the degree of mixing determined using a fluorescence (FL) technique [4]. One of the solutions is marked with fluorescent dye and its concentration profile is visualized according to the FL intensity. The degree of mixing is calculated by the deviation of the obtained concentration profiles from the uniform concentration profile. Ichiyanagi investigated the mixing and chemical reaction fields in a microchannel, and indirectly evaluated the local mass flux distribution based on the concentration gradient measured by LIF and μ-PIV [5]. Kamholz et al. [6], Ismagilov et al. [7] and Baroud et al. [8] visualized the chemical reaction area in the microchannel using the fluorescent product by the reaction between two nonfluorescent chemical species. They observed the region of diffusive mixing in the microchannel. However, the local chemical reaction and mixing rates were not evaluated.

Chemiluminescence (CL) is a light emission phenomenon resulting from a chemical reaction. Unlike FL measurement, no light source is required in CL measurement. Chemiluminescence

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Nomenclature

c	concentration, μmol/mm^3
$c_{in,1}$	inlet concentration of luminol, μmol/mm^3
$c_{in,2}$	inlet concentration of hydrogen peroxide, μmol/mm^3
C	normalized concentration of uranine
d	channel width, mm
d_h	characteristic length, (= 4(dt/2(d+t)) mm)
D	mass diffusivity, mm^2/s
I	CL intensity
k	reaction rate constant, (μmol/mm^3)$^{-1}$ s^{-1}
Q	volume flow rate, mm^3/s
Re	Reynolds number, (= $u_{ave}d_h/\nu$)
t	channel depth, mm
u	velocity, mm/s
u_{ave}	average velocity at the outlet channel, mm/s
x	streamwise coordinate, mm
x_0	entrance length, mm
y	spanwise coordinate, mm
Y_1	reaction yield of luminol

Greek symbols

ν	viscosity, m^2/s
τ	residence time, s
τ_d	diffusion time, s
χ	spanwise-summed reaction rate
χ_{mixing}	spanwise-summed mixing rate

has been widely used in analytical chemistry for sensitive and selective analysis. Tsukagoshi et al. proposed the application of CL to the liquid–liquid interface under a laminar flow in a microchannel for chemical analysis, a technique referred to as microchannel chemiluminescence analysis (MCCLA) [9–11].

In the present study, the luminol CL reaction is used to visualize the local chemical reaction and to estimate the local diffusion and mixing rate at the interface between two liquids in a microchannel. Luminol emits blue chemiluminescence when reacting with hydrogen peroxide at the mixing layer. The CL intensity profile clearly shows the mixing layer at the interface between two liquids. The concentration distribution was also obtained by the FL technique. The experimental results are compared with the results of numerical simulation, which involves solving mass transport equations that include a chemical reaction term. By calibrating the CL intensity for the chemical reaction rate estimated through numerical simulation, the local chemical reaction profile can be quantitatively determined from the CL intensity profile. In the present paper, the effect of the chemical species concentrations on the local mixing and chemical reaction was investigated. Consequently, the relationship between the local mixing rate and the chemical reaction rate in the microchannel was estimated.

2. Experimental apparatus and procedures

The luminol CL reaction with hydrogen peroxide is used in this experiment. The chemical reaction path for the luminol CL reaction [12] is as follows:

$$\text{Luminol} + H_2O_2 + 2OH^- \xrightarrow{Cu^{2+}} 3\text{—aminophtalatedianion} + N_2 + H_2O + h\nu \quad (1)$$

Luminol is oxidized in alkaline solution with hydrogen peroxide to 3-aminophtalatedianion and nitrogen, which produces blue emission (λ = 420–460 nm). The CL of the luminol reaction is activated by a catalyst. In the present study, Cu(II) was used as the catalyst.

A schematic diagram of the microchannel chip is shown in Fig. 1. The microchannel was cast in a polydimethylsiloxane (PDMS) chip with a thickness of 3 mm. The channel length from the junction to the inlets and outlet was 15 mm. The channel width d was 200 μm, and the channel depth t was 50 μm. The PDMS chip was bonded with a cover glass 170 μm in thickness by bringing both surfaces into contact. An acrylic-resin base plate was attached to the rear surface of the PDMS chip. The two reagent solutions were delivered into the microchannels by syringe pumps (KD Scientific KDS210 and Hamilton 17010TLL 10 μl). The average velocity u_{ave} was obtained by dividing the volume flow rate Q by the cross-sectional area of the microchannel, i.e., $u_{ave} = Q/(d\,t)$.

In the present study, CL and the FL images were observed sequentially by changing the optical unit of the inverted microscope. Therefore, the CL reagents and a fluorescent dye were contained in the same solution. Fig. 2(a) and (b) schematically depict the configurations of the experimental system for CL and FL measurements, respectively. Images were obtained using an EM-CCD camera (Hamamatsu Photonics, ImagEM C9100-13) mounted on an inverted microscope (Olympus, IX71). The pixel resolution of the camera was 512 × 512 pixels. A 20× magnification objective lens (N.A. = 0.45, LUCPLFLN20×) was attached to the microscope.

Chemiluminescence images were observed directly through the microscope, as shown in Fig. 2(a). The electron multiplication factor of the EM-CCD camera was set to 100–210 times with an exposure of 10–15 s, due to the extremely weak CL intensity. The fluorescent uranine dye absorbed excitation light from a mercury lamp. Uranine was excited by blue light (485 nm) and emitted green light (515 nm). Fluorescence images were selected through a mirror-filter unit (Olympus, U-MWIBA2) and were recorded by the EM-CCD camera, as shown in Fig. 2(b).

Table 1 lists the compositions of the CL and fluorescent compounds used. The reagent of inlet 1 was a mixture of luminol and

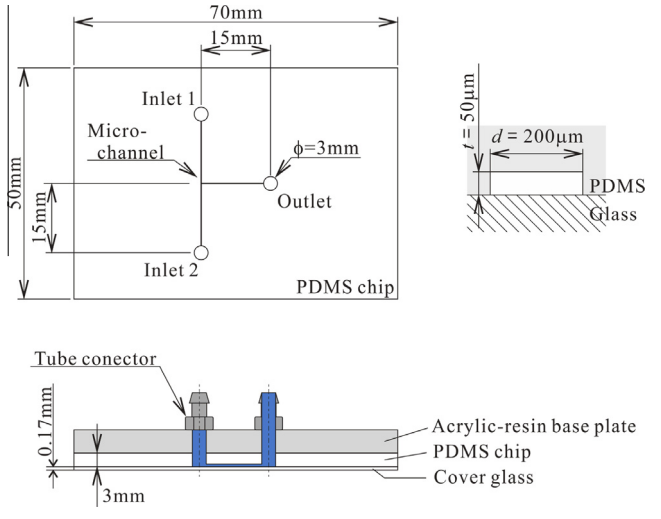

Fig. 1. Microchannel chip. The microchannel is 200 μm in width d and 50 μm in depth t and was cast in a PDMS chip of 3 mm in thickness and covered by a cover glass of 170 μm in thickness. The length of the channel from the junction to inlets and outlet is 15 mm.