Stable Horizontal Interface Formation and Separation of a Water/Oil Flow by Microfluidic Reactor Analyzed by Direct Observation and Numerical Simulation

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Abstract: A microfluidic system with a wide surface area per unit volume has the potential for use in highly efficient chemical synthesis, separation, and extraction. In the case of efficient water/oil separation and material extraction, it becomes important to form a stable two-layer laminar flow interface. Previously, we developed a silicon/glass microfluidic reactor, in which microchannel inner walls were modified to produce hydrophilic/hydrophobic surface. In this work, flow behavior and separation of this microreactor was evaluated. This microfluidic chip made it possible to form a stable two-layer laminar flow interface between a flow of heavier water and lighter hexane, which were introduced into the upper and lower inlets, respectively. The efficiency in separation was examined using water and hexane. Under certain conditions including the pressure difference between the two outlet surfaces, complete phase separation was achieved. This result indicates that the highly efficient separation and stable interface formed by this microfluidic chip can be applied to immiscible liquid-liquid operations with the complete separation of the liquids at the outlets.

Keywords: Microfluidics, microreactor, surface modification, interface, separation, computational fluid dynamics.

INTRODUCTION

In the past decade, applications using microdevices, typically referred to as microfluidic reactors, have had a significant impact on the field of chemical processing and analysis, where the specific behavior of a microfluid is utilized [1-3]. Numerous applications have been proposed in chemical synthesis and analysis, and suitable microdevice fabrication technologies have been developed for these purposes [4,5]. It is quite important to design a microdevice with an understanding of the microfluidic characteristics for a specific application.

In a microchannel, the Reynolds number is generally small and a laminar flow is formed. Because of the wide surface area per unit volume in a microchannel, the interface between laminar flow in a microchannel has attracted much attention in terms of its use in efficient chemical reactions [6,7] and mass transfer [8-10]. In particular, in a material extraction system where a water/oil two-layer laminar flow is applied, a wide interface and the efficient separation of aqueous and organic phases at the outlets are needed. In order to achieve this, it becomes important to stabilize the interface of the two-layer laminar flow.

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[+]Deceased. This paper is dedicated to her memory.

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Several approaches to solving the above problem have been reported, which include maintaining the interface on the guide structure at the bottom of a microchannel using the interfacial tension between the liquid phases [10], and sectionally modifying the microchannel inner wall into hydrophilic and hydrophobic surfaces [11, 12] In these methods, glass plates were mostly used for the microreactors. However, it is generally difficult to bond glass plates together. In addition, in the zone-selective modification of glass microchannel inner walls, a procedure is required for injecting neutral and hydrophobizing solutions under strictly controlled fluid behavior to form a stable side-by-side two-layer laminar flow in the channel.

Previously, we developed a microfluidic extraction system utilizing horizontal interface [13]. This microextractor can be fabricated by means of a simple and easy bonding procedure. First, anodic bonding is carried out using silicon and glass plates for the upper and lower microchannel. Second, it becomes possible to form a hydrophobic self-assembled monolayer (SAM) on one side, by forming an Au thin-film on a silicon microchannel followed by injecting an alkanethiol solution into the entire microchannel after bonding with a glass microchannel. This method does not require special fluid control of the treatment solutions. Using this system, we developed microextraction system for optical resolution. However, detailed study in phase separation efficiency was not performed. A combination study of numerical simulation and direct observation of fluid flow within microchannel become a strong tool for the analysis of fluid

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behabior [14-16]. In this paper, we performed experimental and simulation experiments related to water/oil interface formation and an evaluation of separation efficiency in this microreactor.

Experimental Procedure

Microfluidic reactor was fabricated as previously described. In brief, glass and silicon plates (3 cm x 7 cm x 1 mm) were prepared (Fig. **1A**) and a photoresist mask was applied to the silicon plate. Microchannels (width = 200 μm, depth = 100 μm, length = 40 mm) were fabricated mechanically on both glass and silicon plates (Fig. **1C**) using a Robodrill (FANUC, Japan). The silicon plate was drilled using a diamond drill in 10 μm increments, with a speed of 10 mm/min. The glass plate was drilled at a speed of 20 mm/min. In order to form an Au thin-film only on the inner wall of a microchannel in the silicon plate, a Ti thin-film (about 30 nm thickness) was formed on the masked silicon plate by electron beam evaporation, followed by Au thin-film formation (about 50 nm thickness), also by electron beam evaporation. Finally, the photoresist on the silicon plate was removed by treatment with acetone. The glass plate was cleaned with *Piranha* solution and bonded to the above silicon plate by means of anodic bonding (500 ^{o}C, 600V, 1 hour, Fig. **1G**). An ethanol solution of 1 mmol/L octadecanethiol was injected into the microchannel with a fluid velocity of 1 μl/min for 12 hours. Through the above procedure, a zone-selectively hydrophobized microreactor was fabricated, as shown in Fig. (**2**). The hexane contact angle of another octadecanethiol SAM on a flat silicon plate formed by a similar method (hydrophobic) was determined to be about 30°-35°, and that on a glass plate (hydrophilic) was determined to be about 95°-110° [17].

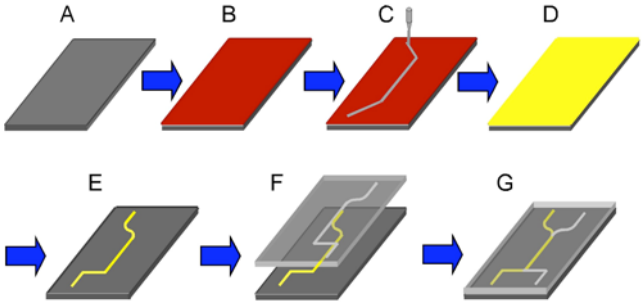

Fig. (1). Fabrication of the silicon-glass microreactor. Only the inner wall of the microchannel of the silicon plate is coated with Au. (**A**) silicon plate (**B**) coated with photoresist (**C**) mechanical fabrication of a channel (**D**) coated with Ti followed by Au (**E**) removing the photoresist (**F**) anodic bonding with a glass plate (**G**) fabricated microchannel.

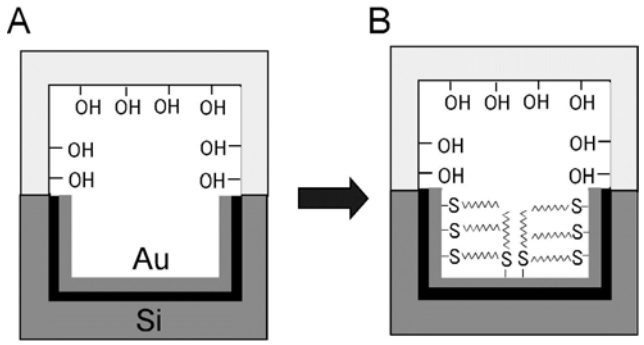

Fig. (2). Zone-selective modification of a silicon-glass microchannel. (**A**) before and (**B**) after modification by treatment with an octadecanethiol solution.

Fig. (**3**) shows the fabricated microreactor. Water and hexane were injected into a glass-side (upper) inlet and a silicon-side (lower) inlet, respectively, by a programmable syringe pump. For observation of fluid behavior, a confocal fluorescence microscopy system (Nikon, Japan) was utilized using an aqueous solution of 50 μmol/L fluorescein instead of pure water. A computational fluid dynamics (CFD) simulation was performed using FLUENT 6.2 (FLUENT Inc., U.S.A.), as previously described [15, 16, 19].

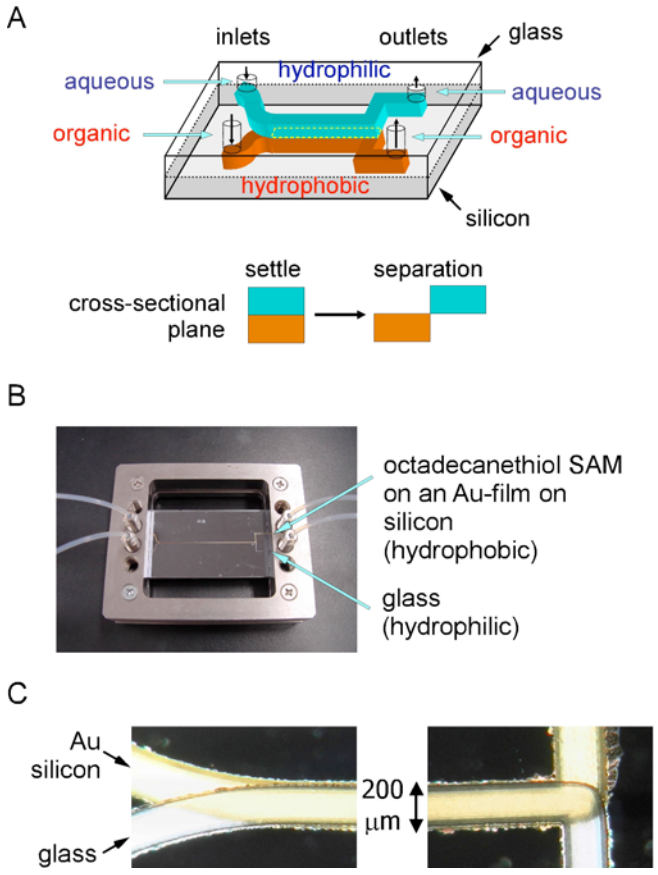

Fig. (3). The fabricated microchannel. (**A**) scheme for the microchannel (**B**) Photograph of the fabricated microchannel with Teflon tubes® (**C**) magnified picture at the merging point and the split point.

RESULTS AND DISCUSSION

Fig. (**4**) shows confocal fluorescence microscopy observation results for a water/hexane two-phase flow in the fabricated microchannel. The flow rate for both water and hexane was 1 μl/min, and the average velocity of each liquid in the inlet was approximately 0.1 m/s. A stable two phase flow and an interface were formed through the channel from the merging point to the split point.

Table **1** summarizes the experimental results concerning the relationship between flow rate and fluid behavior. For comparison, another silicon/glass microreactor was prepared

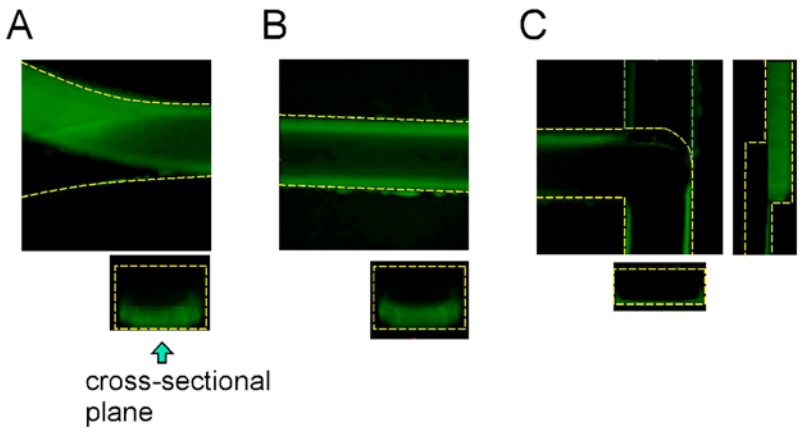

Fig. (4). Observation of a stable interface between a laminar flow of water and hexane. (**A**) at the merging point of the water and hexane (**B**) middle part of the microchannel (**C**) at the split point near the outlets.

Table 1. Effects of Hydrophobic Modification on the Formation of a Stable Laminar Flow Interface. "OK" Denotes Stable Laminar Flow and "NG" Slug Flow

flow rate for each liquid [μl/min]	0.01	0.05	0.1	0.5	1	5	10	50	100
with octadecanethiol SAM	OK	OK	OK	OK	OK	OK	OK	OK	OK
without octadecanethiol SAM	NG	NG	NG	NG	NG	NG	NG	NG	OK
Reynolds number (water) [-]	0.001	0.006	0.01	0.06	0.1	0.6	1	6	10
Capillary number [-]	2E-7	8E-7	2E-6	8E-6	2E-5	8E-5	2E-4		
Weber number (water) [-]							2E-4	5E-3	2E-2

having the same shape, but without the zone-selective modification. In the unmodified microreactor, a stable laminar flow was not formed except for the case of a very rapid flow rate; slug flow occurred in most cases. On the other hand, the zone-selectively modified microreactor supported a stable laminar flow over all flow rates.

Table **1** also shows the Reynolds number *Re*, Capillary number $Ca = \frac{\mu U}{\gamma}$, and Weber number $We = \frac{\rho U^2 D}{\gamma}$. The latter two non-dimensional numbers express the characteristics of two-layer laminar flow of liquids with the interfacial tension by comparing viscous force, inertial force, and interfacial force. *Ca* is used in the case of *Re*<1, while *We* is used in the case of *Re*>1. When these values are more than unity, the viscous force or the inertial force exceeds the interfacial force, and the interface is deemed to be stable. The results shown in Table **1** indicate that the interface is stable for all flow rates because *Ca* or *We* is less than unity. This is consistent with the fact that the unmodified microreactor could not support a stable laminar flow. It also indicates that the zone-selective modification was effective for stabilizing laminar flow.

The above observation was carried out with the glass microchannel on the downside because of restrictions imposed by the confocal fluorescence microscopy system. In the present work, the value of capillary constant $a = \sqrt{\frac{2\gamma}{g\rho}}$, which is used for the evaluation of gravity force and interfacial force effects [18], is about 5 mm (γ = 0.05 N/m, $\Delta\rho$ = 1000 kg/m^3 - 660 kg/m^3= 340 kg/m^3). This value is much larger than the width and depth of the microreactor, and suggests that the effect of gravity is negligible. Thus, it can be speculated that a stable two-layer laminar flow is formed, even if the microreactor is upside down and this microreactor is very effective for supporting a stable water/oil interface.

The separation performance of water and hexane at the outlets was next examined. Colored water was used for visibility and the liquid in the Teflon® tubes (inner diameter = 750 μm, outer diameter = 1/16 inch) connected to the outlets was observed. Since slug flow was observed when the separation was not perfect, separation efficiency was evaluated by the ratio of the length between water and hexane. Fig. (**5**) shows the results. Ideally, 100% water and 100% hexane should be discharged from the glass-side and silicon-side outlet respectively. The experiments showed that 90% of the liquid from the glass-side outlet was water, while hexane from the silicon-side outlet was only 70% in most cases. In this experiment, the heights of the edges of the 10 cm long tubes were set to be the same.

Separation efficiency may be affected by the pressure difference between the outlets. Thus, another experiment was performed with the edge of the silicon-side outlet tube raised 10 cm higher than the edge of the water-side outlet tube. As a result, as shown in Fig. (**6**) by the upward arrow, the percentage of hexane from the silicon-side outlet was considerably increased, especially at low flow rates. The pressure

difference between silicon- and glass-side outlets in this case was estimated to be about 150 Pa for a flow rate of 1 μl/min. This value is larger than the pressure drop in the microchannel, estimated to be about 90 Pa. This dominance of the outlet pressure difference could provide an explanation for the above difference in separation performance. The separation efficiency of water from the glass-side outlet was as good as the case where the outlet tube heights were the same. Thus, the separation of a water/hexane flow was almost perfect in the case of lower flow rates. It is likely that separation performance is also affected by small differences, such as the microreactor size and the degree of hydrophobicity produced in the fabricating process. It would be quite important to fabricate and handle microreactors precisely in order to achieve a perfect separation.

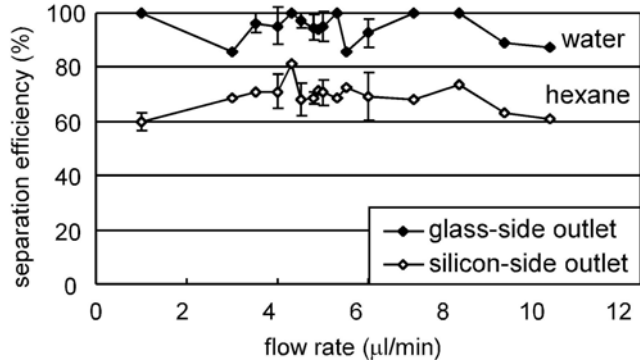

Fig. (5). Separation efficiency for water and hexane.

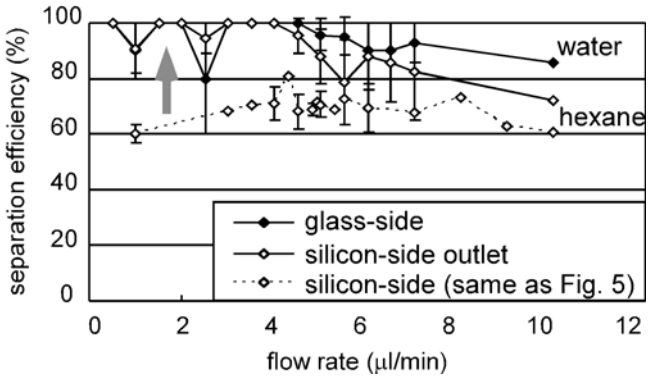

Fig. (6). Separation efficiency for water and hexane after raising the outlet tube a distance of 10 cm. Dashed line is the result when the outlet tube height was the same.

Next, we performed a computational fluid dynamics (CFD) simulation for a water/hexane two-phase flow. Fig. (**7**) shows the dimensions of the model microchannel used for the simulation. Based on the experimental data, the contact angle of hexane on the microchannel wall in the water-hexane mixture was varied over eight pairs, and water (ρ= 998 kg/m^3, μ= 1.00 x 10^{-3} Pa· s) and hexane (ρ= 660 kg/m^3, μ= 0.32 x 10^{-3} Pa· s) were assumed to be introduced into the microchannel with fluid velocity of 0.1 m/s. The effect of gravity on horizontal two-layer flow was examined by simulation assuming that water, with a higher density than hexane, was introduced into the upper channel. The VOF (Volume of Fluid) scheme was used for the calculation.

Fig. (**8**) shows the simulation results for a water/hexane two-phase flow. θ in the figure is the contact angle of hexane on the modified substrates. When the upper channel walls become more hydrophilic, and when the lower channel walls become more hydrophobic, stable two-phase laminar flow is formed and good separation is achieved. This indicates that the microreactor fabricated in this work (θ = 30°-35° on the hydrophobic walls and 95°-110° on the hydrophilic walls), forms a stable two-layer laminar flow and that separation is achievable over a range of contact angles, as in the case of octane [19].

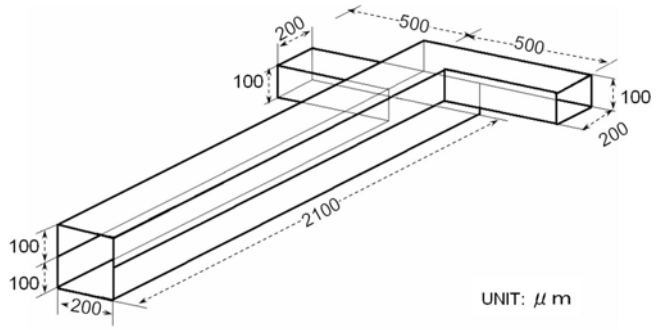

Fig. (7). Dimensions of the microchannel used in the simulation. Numerals are in units of μm.

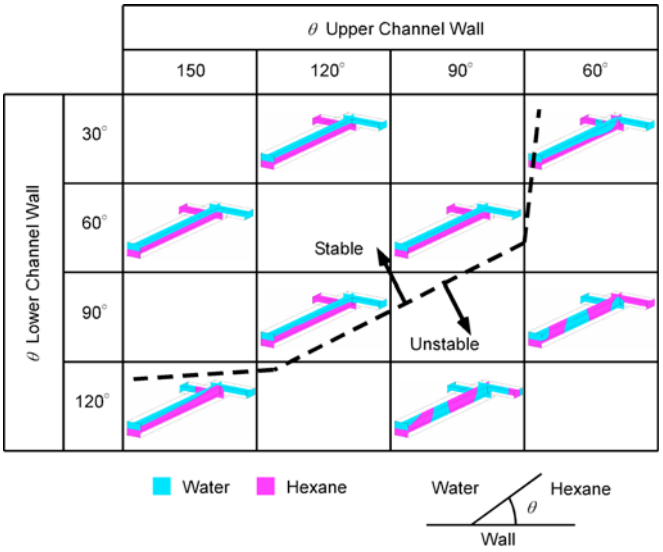

Fig. (8). Simulation results related to the stability of a water/hexane laminar flow and separation in microchannels with various contact angles. The broken line indicates an approximate boundary between the stable and unstable flow regimes.

CONCLUSIONS

A zone-selectively hydrophobized microreactor, the fabrication of which was facile, was developed for the purpose of forming a stable water/oil interface and separation. The hydrophobizing of selected walls was achieved using a silicon plate with an Au thin-film on a microchannel inner wall bonded with a glass plate followed by the injection of an octadecanethiol solution into the microchannel. A stable two-layer laminar flow of water/hexane was experimentally observed, and was in agreement with the prediction by CFD simulation. As a result of discussions concerning the effects of gravity by using a capillary constant, it was found that gravity has little effect on this stable interface in the zone-

selectively modified microchannel. For the separation of water/hexane at the outlets, a perfect separation was achieved under specified conditions. However, the findings show that the pressure difference between the outlets affects separation performance. This implies that care needs to be exercised in the fabrication and treatment of microreactors when a perfect separation needs to be achieved.

In conclusion, the microreactor which was developed by our laboratory, was proved to be efficient phase separator by the combination study of direct observation and numerical study. The stable interface and high separation efficiency realized in this work could be applied to areas such as measurements of interfacial tension, material extraction, and analysis of partition coefficients.

ACKNOWLEDGEMENTS

This research was partially supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan, Project of Micro-Chemical Technology for Production, Analysis and Measurement Systems.

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Received: May 28, 2011 Revised: June 30, 2011 Accepted: July 02, 2011