Microfluidic Inverted Flow of Aqueous and Organic Solvent Mixed Solution in a Microchannel under Laminar Flow Conditions

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When two solutions are individually fed into two separated microchannels of a microchip that combine to form a single channel of a Y-type microchannel, the flows in the single channel are either parallel for immiscible solutions or initially parallel but become homogeneous through diffusion for miscible solutions. Nevertheless, a new type of microfluidic behavior was seen in the Y-type microchannel that was neither parallel nor homogeneous flow. Water-acetonitrile and acetonitrile-ethyl acetate mixtures, each marked by a distinctive dye, were delivered at the same flow rate into the Y-type microchannel under laminar flow conditions. Under different volume ratio mixtures, the two phases in the single channel were initially observed to flow in parallel but then swapped over to the opposite wall while still retaining parallel flow. We call this type of laminar flow "microfluidic inverted flow".

Key words: microchannel chromatography, tube radial distribution, ternary mixed solution, phase diagram

1. Introduction

The development of micro-total analysis system (μ-TAS) that includes microchip or microfluidic device technology is an interesting aspect of analytical science.[1,2] Microfluidic solvents exhibit various fluidic behaviors in microchannels. Their flow patterns have been examined by varying the channel configuration and flow rate of the solvents, using aqueous–organic solvent mixtures, and introducing specific obstacles into microchannels.[3–5] Fluidic flow of solvents in microchannels is related to separation, diffusion, and reaction of solutes. Information regarding their microfluidic flow and interface formation is important and useful in designing microreactors or μ-TAS.[1–5]

Various types of mixed solutions of aqueous–organic solvents are used in dissolution, cleaning, preservation, and as reaction solvents. Such mixtures are also useful in separation science.[6–8] However, to our knowledge, the use of ternary mixed solvents of water–hydrophilic/hydrophobic-organic solvents has not been examined in detail. When such ternary mixed solvents were fed into the microspace under laminar flow conditions, the solvent molecules radially disperse in the microspace through a phase transformation; this microfluidic behavior we call the "tube radial distribution phenomenon" (TRDP).[9–11]

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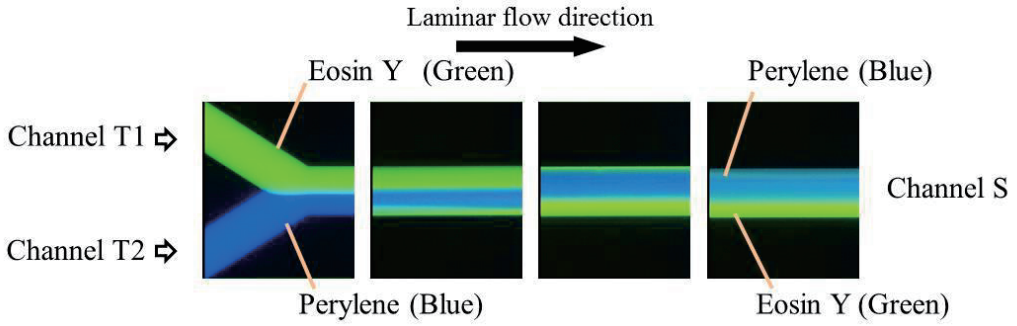

Fig. 1. Typical microfluidic inverted flow observed in channel S of a Y-type microchannel. Channel T1, 2.0 mM Eosin Y dissolved in water-acetonitrile (20:30, v/v) and channel T2, 0.2 mM perylene dissolved in acetonitrile-ethyl acetate (20:30, v/v). Flow rate, 10 μL min^{-1} each at 20°C.

2. Experimental

In this study, the microfluidic behavior of two combining mixtures, water–acetonitrile and acetonitrile–ethyl acetate, was examined under the fluorescence of dyes, Eosin Y (green) and perylene (blue), in the respective solutions. A microchip fabricated with a Y-type microchannel (Microchemical Technology, Kanagawa, Japan) was used, in which two separated channels, labeled channels T1 and T2, combined to form a single channel, labeled channel S (see Fig. 1).

Each channel was 100 μm wide × 40 μm deep. The two mixtures to be combined were fed into the two separated channels. In the single channel, the combined mixture developed a specific fluidic behavior, *i.e.*, microfluidic inverted flow, that depended on the solvents.

Water was purified with an Elix 3 UV system (Millipore Co., Billerica, MA). All reagents used were obtained commercially and were of analytical grade. Perylene, Eosin Y, acetonitrile, and ethyl acetate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The water– acetonitrile mixture (20:30 volume ratio) containing 2.0 mM Eosin Y and acetonitrile–ethyl acetate mixture (20:30 volume ratio) containing 0.2 mM perylene were fed at the same flow rate into channels T1 and T2, respectively, using a microsyringe pump. A microscope–CCD camera system was set-up to observe fluorescence from the dyes, Eosin Y and perylene, which emit light at 470 nm (green) and 550 nm (blue), respectively. The fluorescence was monitored near the combining point and in channel S using a fluorescence microscope (BX51; Olympus, Tokyo, Japan) equipped with a Hg

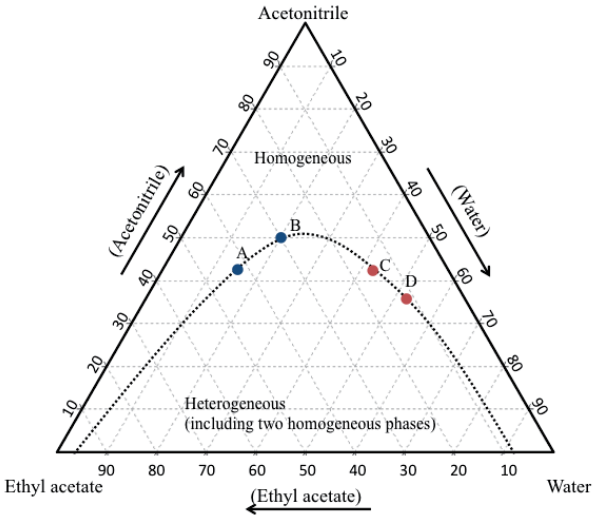

Fig. 2. Phase diagram of ternary mixed solvents of water-acetonitrile-ethyl acetate mixture. The curve meant the boundary between homogeneous (single phase) and heterogeneous (two phases). The component ratios of water-acetonitrile-ethyl acetate; A; 14:43:43 B; 20:50:30, C; 43:43:14, and D; 52:37:11. 20°C.

lamp, a filter (U-MWU2, ex 330–385 nm, em > 420 nm), and a CCD camera (JK-TU53H).

The blue and green fluorescence images give a clear separation of the two flows. A distinctive feature to be noted is the microfluidic inverted flow in the Y-type microchannel with the water–acetonitrile and acetonitrile–ethyl acetate mixed solutions (Fig. 1); the flow conditions are indicated in the figure captions. This inverted flow was unobserved with water and water, acetonitrile and acetonitrile, ethyl acetate and ethyl acetate, water and acetonitrile mixtures, as well as acetonitrile and ethlyl acetate mixed solutions (miscible solutions); each of these combinations initially exhibited parallel flow and then homogeneous flow. The immiscible solutions of water and ethyl acetate mixtures produced parallel or sluggish flow, never inverted flow, in the Y-type microchannel. Only the ternary mixed solvent of water, acetonitrile, and ethyl acetate could bring about "microfluidic inverted flow". The information will be useful for clarifying creation of "microfluidic inverted flow" in the future.

Here, with respect to our previous work on ternary mixed solvents of water-acetonitrile-ethyl acetate,[11] we tentatively examined the composition ratios near the boundary curve in the phase diagram of the water-acetonitrile-ethyl acetate mixed solution (Fig. 2). The compositions of the water-acetonitrile-ethyl acetate mixed solutions were A; 14:43:43, B; 20:50:30, C; 43:43:11, and D; 52:37:11. The water-acetonitrile and acetonitrile and ethyl acetate mixed solutions were mixed so that compositions of A–D were produced in channel S. Mixed solutions with compositions A, B, and C (organic solvent-rich solutions) showed microfluidic inverted flow, whereas those of D (water-rich solutions) exhibited a parallel-to-homogeneous flow evolution. Reasons for the microfluidic inverted flow for these mixed solutions remain unclarified.

3. Results and Discussion

3.1 *Effects of flow rates and channel lengths on the microfluidic inverted flow*

The conditions are given in the captions. The fluorescence images were observed around the mixing point and in channel S at distances 1, 2, and 3 cm from the mixing point with flow rates 10, 20, and 100 μL min^{-1} (Fig. 3). As flow rate increased, we observed

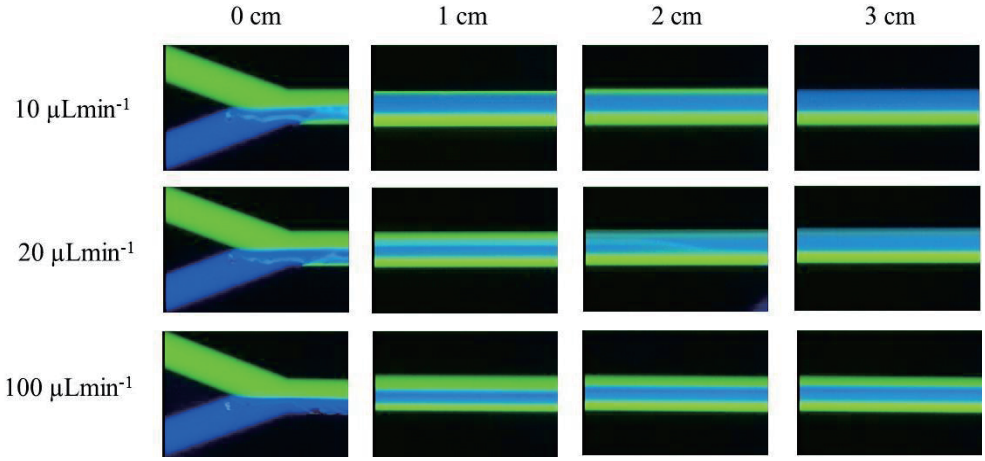

Fig. 3. Effects of flow rate on the microfluidic inverted flow in channel S. Conditions in channels T1 and T2 are the same as in Fig. 1. 20°C.

various stages of inverted flow in the channel. Fig. 4 shows the inverted flow in a long single microchannel in a Y-type microchip. We also observed inverted flow in a long wooden microchannel.

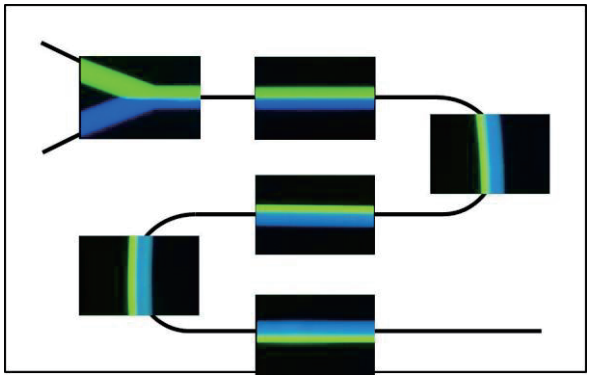

Fig. 4. Effect of single-microchannel length on the microfluidic inverted flow in channel S. Conditions in channels T1 and T2 are the same as in Fig. 1. 20°C. The single microchannel length is 12 cm and included the two bends.

3.1 *Microchip with three connecting Y-type mixing points*

We had a microchip that included three connecting Y-type mixing points (Microchemical Technology, Kanagawa, Japan) (Fig. 5). The water-acetonitrile and acetonitrile-ethyl acetate mixed solutions were fed in the microchannels *via* two of the Y-type microchannels (Fig. 5); see caption for the conditions. Downstream from the first two Y-type mixing points, microfluidic inverted flows formed in the individual channels; the composition ratio of the water-acetontitruile-ethyl acetate was 20:50:30 in these sections of the channels. Subsequently, the two inverted flows were mixed at the third Y-type mixing point, from which TRDP formed in the microchannel; the composition ratio after mixing was 20:50:30 in this section channel. This unique microfluidic flow, shown

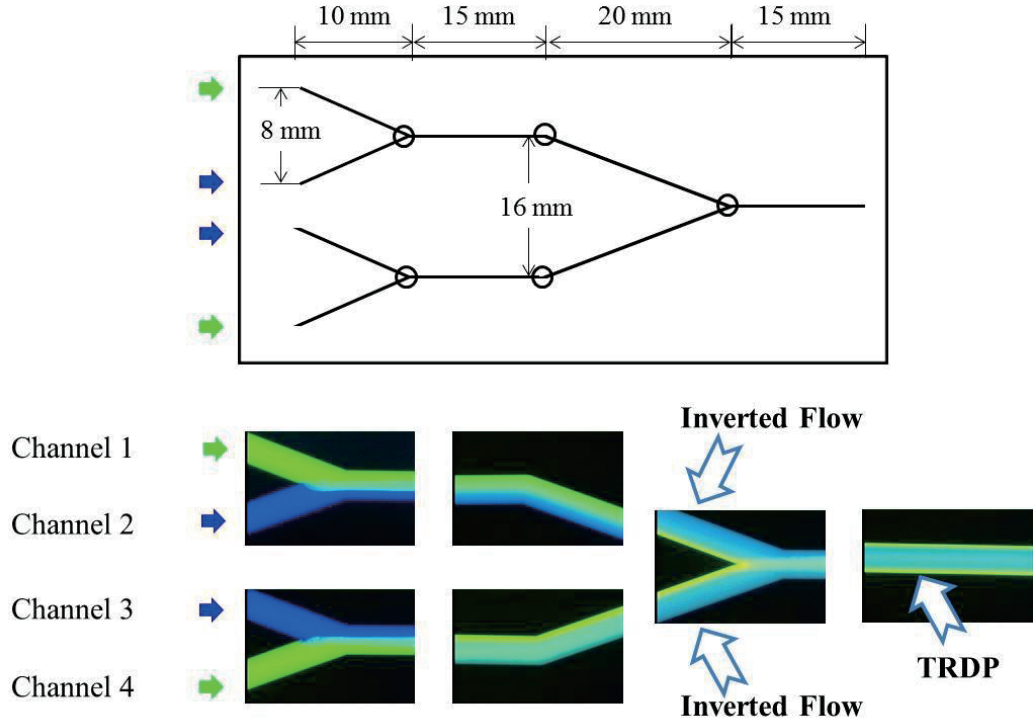

Fig. 5. Schematic diagram of a microchip with three Y-type mixing points in the microchannel. Conditions in channels 1 and 4 are the same as in channel T1 of Fig. 1; channels 2 and 3 have the same conditions as for channel T2 in Fig. 1. Flow rate is 2.0 μL min^{-1} each at 20°C.

in Fig. 5, has never been created in a microchannel by any other technique. Such a novel microfluidic flow pattern or liquid-liquid interface formation might lead to innovation of separation, extraction, mixing, and chemical reaction in a microspace.

4. Summary

In conclusion, ternary solvents of water–acetonitrile–ethyl acetate mixtures in a single channel were prepared by combining a water–acetonitrile mixture and an acetonitrile–ethyl acetate mixture fed from two separated channels in a Y-type microchannel of a microchip. A microfluidic inverted flow was a specific and interesting flow seen from the mixing of particular compositions of solvents in the single channel. This unique inverted flow was produced with the ternary mixed solvent of combining the two mixtures. The specific microfluidic flow was not observed using two-component solvents, *i.e.*, a water–acetonitrile mixture or a water–ethyl acetate mixture. The data of the inverted flow, visualized under dye floresence are expected to be useful in developing a mixing technique to create a phase interface and a chemical reaction space in the microspace of a microchip.

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