Interfaces

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Countercurrent Laminar Microflow for Highly Efficient Solvent Extraction**

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Countercurrent flows are commonly used in various chemical fields. In conventional macroscale devices, countercurrent flows are accompanied by droplets from breakup due to high shear stress at the interface. Parallel countercurrent laminar flows are more desirable from the viewpoint of allowing better design and control of chemical processes in a microchannel. Herein, we report countercurrent laminar microflow under conditions that give a low Reynolds number *Re* ($Re < 2.3$) in a microchannel. To produce the countercurrent flow of aqueous and organic phases, we selectively modified the lower half of a microchannel wall with a hydrophobic group while the upper half was kept hydrophilic. The flow-rate ratio between the two phases was investigated and a wide operational range for the countercurrent flow was verified. The countercurrent flow was applied to a solvent-extraction process. While conventional microscale extractions with cocurrent multiphase flow or droplets can reach a theoretical plate number of only unity, a higher theoretical plate number is expected in an extraction that uses countercurrent microflow. We found a theoretical plate number of 4.6 for the extraction of a cobalt complex in an aqueous–toluene countercurrent microflow.

Investigations on microscale techniques based on pressure-driven microflows have been advancing rapidly.[1–7] By using the characteristics of a microspace, parallel cocurrent microflow of immiscible phases can be formed by a pressure-driven flow. As flows in a microspace are characterized by a low *Re*, the cocurrent microflow can be considered as laminar flow. A network based on cocurrent microflow is an effective tool for integrating microchemical processes because sequential contact and separation of immiscible phases can be freely designed in a laminar-flow regime. In this way, we can combine various microunit operations (MUO) under continuous-flow conditions, a method we have named continuous-flow chemical processing (CFCP).[8–11]

Solvent extraction is one of the most important separation methods and some solvent-extraction microsystems have been reported. TeGrotenhuis et al. reported one based on a porous polymer membrane to stabilize the liquid–liquid interface.[12] That system used the hydrophobic character of the membrane to support the organic phase. However, the effect of mass-transfer residence at the membrane, caused by, for example, membrane thickness and porosity, should be considered. Shaw et al. reported a solvent-extraction microsystem in which two microchannels were fabricated on a pair of upper and lower plates and made contact with a slight shift of an axis.[13] Their system had only a small interfacial area, although a large interfacial area is more effective in mass transfer. We have reported cocurrent solvent extraction in microchannels with a guide structure and a small interfacial area.[8] These systems are effective from the viewpoint of reducing the time needed for solvent extraction as they are two orders of magnitude faster than conventional macroscale systems. However, from the viewpoint of recovery efficiency, cocurrent solvent extraction on microscale (Figure 1 a) can do no better than a system with a theoretical plate number of unity.

If liquid–liquid countercurrent microflow is possible, it is expected to be applicable to high-recovery solvent extraction on the microscale as the aqueous phase flows from the downstream of the organic phase and dissolves material (Figure 1 b). In conventional macroscale devices, counter-

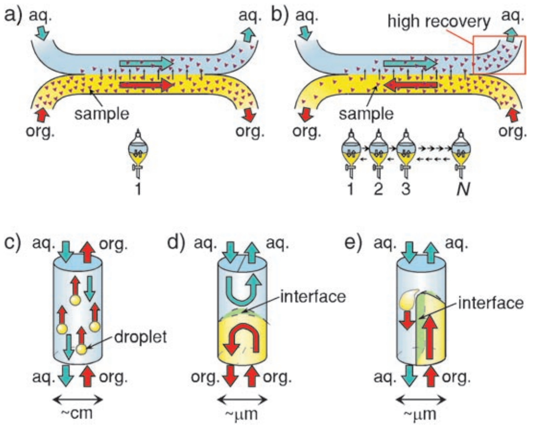

Figure 1. Schematic diagrams of a) cocurrent microextraction, b) countercurrent microextraction, c) countercurrent flow in conventional devices, d) collision of two phases in an ordinary microchannel, e) droplet generation because of breakup due to high shear stress in an ordinary microchannel. In (a) and (b), the theoretical plate number (*N*) is indicated.

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current flow is accomplished by gravitational segregation involving droplets (Figure 1 c). Although countercurrent flow has attractive features, the two phase separation technologies used in macroscale experiments cannot be applied at the microscale. In microfluidic systems, viscosity and surface wetting are more effective at controlling flow than gravity and inertia. Therefore, in such systems, laminar countercurrent flow is more feasible than microdroplet countercurrent flow. Although laminar flow has a disadvantage in mixing compared to a droplet system,[14] the laminar countercurrent flow is advantageous in better design and control of chemical microprocesses.

Gas–liquid countercurrent microflow is brought about by selective surface modification.[15] As detailed in the Supporting Information, the dominant forces involved are the interfacial tension and the viscous force of the aqueous phase, the viscous force of the gas phase being negligible. In the case of liquid–liquid countercurrent microflow, the interfacial tension and viscous forces of both phases play important roles. Therefore, liquid–liquid countercurrent microflow cannot be easily established. In an ordinary microchannel, countercurrent flow cannot occur because the two phases collide (Figure 1 d) and high shear stress at the liquid–liquid interface causes breakup (Figure 1 e). To form countercurrent microflow, the aqueous solution must flow along one side of the channel and the organic solution must flow along the other side without breakup.

Herein, we report a laminar countercurrent microflow system with a low *Re* on a glass microchip, which was obtained by selectively modifying the lower half of a microchannel with a hydrophobic group, and which was applied to recover a cobalt complex.

Previous reports have proposed selective surface modifications of glass microchannel walls.[15–17] Such methods are very effective because they exploit interfacial tension and wetting, which are influential factors in microchannels. Figure 2 a illustrates a microchannel that has undergone selective surface modification by using procedures reported previously.[16] The upper half of the microchannel for aqueous-phase flow was carefully washed with sodium hydroxide solution to obtain a hydrophilic surface while the lower half for the organic-phase flow was modified with octadecyltrichlorosilane (ODS) to obtain a hydrophobic surface. In this way, we were able to create countercurrent microflow with a low *Re*, 0.16 for water and 0.19 for butylacetate, as shown in Figure 2 b. The absence of color change between the inlet and outlet of each microchannel is evidence of a two-phase separation.[18]

We investigated the range of two-phase flow rates that permitted separation (Figure 3). Without surface modification, two phases can be separated only under the conditions indicated by the green line. However, in a microchannel with a selectively modified surface, there is a wide range of conditions that allow a separation with cocurrent (yellow) and countercurrent flow (purple).

In countercurrent flow, the pressure balance between the two inlets and the two outlets is very important. To investigate this issue, we measured the interfacial tension and the contact angles. The interfacial tension between water and butylacetate is 13.4 mN m^{-1} at 296 K (pendant-drop method). The contact angles of water and butylacetate on a bare glass surface are 4.1 and 2.7°, respectively, while those on an ODS-modified glass surface are 106.4 and 6.8°, respectively. The high value of the contact angle of water on the ODS-modified surface means that when the water flow has a positive pressure relative to the organic flow and intrudes onto the hydrophobic ODS-modified surface, the capillary pressure (Laplace pressure) compensates for the pressure difference to maintain the interface position.

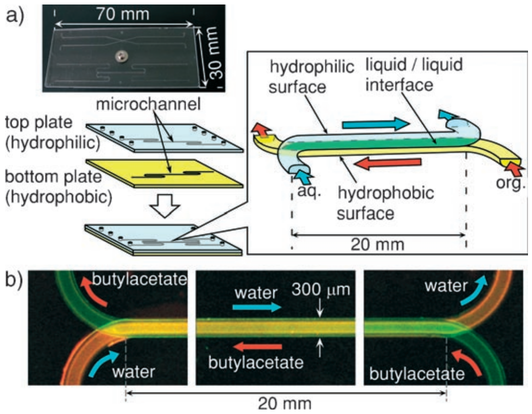

Figure 2. a) A microchip that has undergone selective surface modification. The microchannel has a depth of 200 μm, a width of 300 μm, and a liquid–liquid contact length of 20 mm. The upper half of the microchannel wall is hydrophilic and the lower half hydrophobic. The green area indicates the liquid–liquid interface. b) Fluorescence microscope images of the countercurrent microflow formed in the microchannel illustrated in (a). The aqueous phase (red) is a red-fluorescent nanoparticle dispersion and the organic phase (green) is lipophilic fluorescein in butylacetate; each solvent was saturated with the other. At the liquid–liquid contact area, the colors of the two phases are mixed optically and the fluid is yellow.

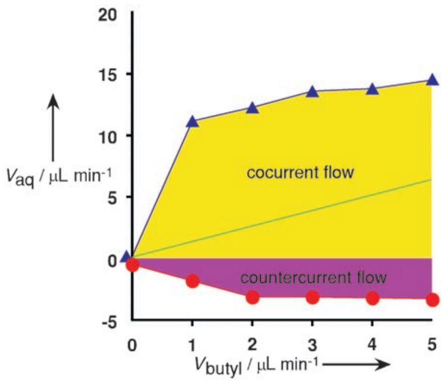

Figure 3. Phase-separation conditions at various aqueous (V_{aq}) and butylacetate (V_{butyl}) flow rates. The green line shows the conditions in the nonmodified microchannel. The blue triangles show the limit of the phase separation for cocurrent microflow and the red circles the limit of the phase separation for countercurrent microflow in a selectively surface-modified microchannel.

We applied countercurrent microflow to a solvent extraction on the microscale, specifically, cobalt tri(2-nitroso-5-dimethylaminophenolate) in toluene (10 μM) was extracted with water. The cobalt complex was synthesized by using a reported procedure.[19] The distribution coefficient (concentration of the cobalt complex in the aqueous phase/concentration of the cobalt complex in the organic phase) is 1.54. The concentration of the cobalt complex in the two phases was determined before, during, and after extraction by thermal lens microscopy (TLM).[20] TLM can measure low-concentration samples with a short optical length, which is desirable for in-channel determination. The detection points were 10 mm away from the confluence of the two phases at the center of the microchannel. The recovery efficiency of the extraction was measured as a function of the flow rates of the two phases. The aqueous flow rate was set to be equal to the organic flow rate and the flow rates of the two phases were varied from 0.15 to 1.0 μL min^{-1}. As detailed in the Supporting Information, the TLM signal intensity in the two phases as a function of the flow rates indicates that the cobalt complex is extracted from toluene into water.

As the TLM signal intensity is proportional to the sample concentration, we calculated the concentration, percent extraction, and the theoretical plate number from the difference of this intensity in toluene before and after extraction (1.68 mV and 22.9 μV). The maximum percent extraction is estimated to be 98.6%, thus confirming that countercurrent extraction on the microscale with low distribution coefficients and high recovery efficiency is feasible. The theoretical plate number indicates how many repetitions of phase separation and confluence are necessary for the desired percent extraction. By using the equation given in the Supporting Information, we calculated this number. Figure 4 shows it as a function of the flow rate. The maximum theoretical plate number is estimated to be 4.6. This figure means that carrying out one countercurrent microextraction has the same effect as carrying out 4.6 cocurrent microextractions. Countercurrent laminar microflow is expected to be applicable to enrichment processes for various environmental analyses and biomolecule separations.

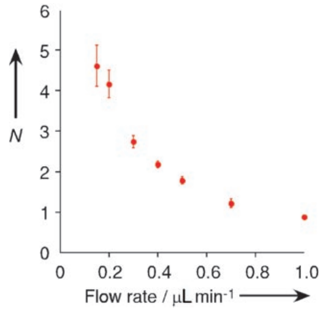

Figure 4. The theoretical plate number (N) as a function of the flow rate.

In summary, we have described a countercurrent laminar-flow microsystem that employs selective surface modification of a microchannel. The extraction of a metal chelate was demonstrated with high recovery efficiency. Because countercurrent laminar microflow can now be realized in a microspace, a variety of applications that combine such flow with CFCP become possible.

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