Electronic Supplementary Information

Countercurrent Liquid-Liquid Extraction on Paper

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Reagents and consumables

Grade 1 chromatography paper (Whatman, Maidstone, England) was used to make the paper devices. Alkyl ketene dimer (AKD) was kindly donated to us by Ashland Inc. (Tampere, Finland) and was dissolved (5 g/L) in hexane (Biosolve B.V., Valkenswaard, The Netherlands). Distilled water purified using a Sartorius Stedim Arium 611VF system (referred to ultrapure water from here on) and 1-octanol (Sigma Aldrich, Steinheim, Germany) were used as the two immiscible phases. Hydrophobic blue ink from a permanent marker (Staedtler, Nuremberg, Germany) was deposited onto a piece of paper and later extracted into an aliquot of octanol until a satisfactory dark color was obtained. Hydrophilic yellow food dye concentrate (E102/E124) or hydrophilic blue food dye concentrate (E131) was added to ultrapure water until a satisfactory intensity was obtained. Basic fuchsin (Sigma Aldrich, Steinheim, Germany) was dissolved in octanol until a saturated, dark pink solution was obtained. Concentrated hydrochloric acid (HCl, Merck, Darmstadt, Germany) was diluted in ultrapure water to a concentration of 1 M. Note: all procedures and experiments with either hexane or 1-octanol were conducted in a fume hood.

AKD-coating procedure

A strip of paper was fully immersed into the 5 g/L hexane solution of AKD and dried in air. This step was then repeated. After the second treatment, the dried paper was put into an oven at 100^{o} C for at least 15 minutes. Heating up the paper led to melting and spreading of the AKD material over and through the paper, which in turn increases the binding to hydroxyl groups on the cellulose fibers and thus the hydrophobicity of the paper [1].

Experimental setup

The paper setup which was used to demonstrate the challenges in setting up a side-by-side (countercurrent) flow on paper is depicted in Figure S1. The design is simple, consisting of a single channel cut from untreated paper, with two inlet pads and two outlet wicks (schematically depicted as triangles). The paper structure was cut from a rectangular paper strip to the desired shape, and affixed to a piece of adhesive tape. Source pads (rolled-up tissue) were placed on top of the inlets, and pieces of paper acting as wicks on the outlets to maintain solution flow. Pads and outlet wicks could be shifted to different positions as desired. Outlet wicks were replaced regularly to maintain the capillary pressure.

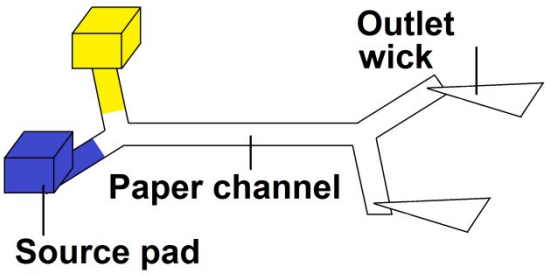

Figure S1. Configuration of paper setup for demonstrating the challenges in creating a side-by-side (countercurrent) flow on paper.

The paper setup which was used for a two-phase countercurrent flow on paper is depicted in Figure S2. The figure demonstrates as well how the setup is assembled. A zig-zag channel was cut from untreated paper; a straight channel was cut from AKD-coated paper. The two channels were superimposed and aligned, and then affixed to a piece of adhesive tape (sticky side up) to fix the alignment. Next, the untreated channel was wetted with ultrapure water. Afterwards, the AKD-coated channel was wetted with octanol. Source pads with water or octanol solutions could then be placed onto the inlets of the channels, whereas triangular wicks were placed on the outlets of the channels as sinks for the solutions in the channels and to maintain flow. The wicks at the outlets were replaced regularly during an experiment.

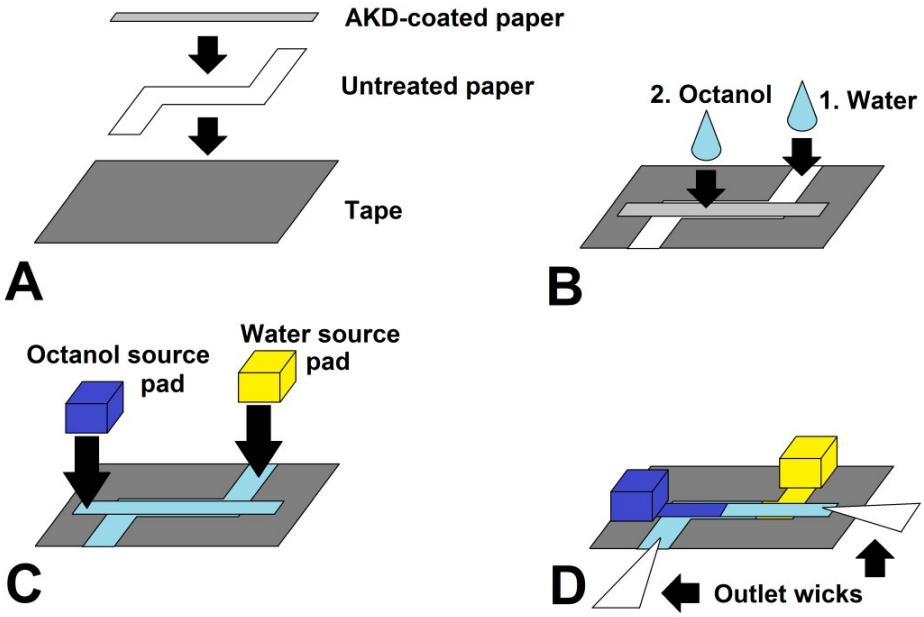

Figure S2. Configuration and assembly of the setup for paper-based two-phase countercurrent flow. (A) An untreated and an AKD-coated channel were combined on a piece of tape. (B) First, the untreated channel was wetted with water, then the AKD-coated channel was wetted with octanol. Afterwards, (C) source pads with test solutions of water and octanol and (D) outlet wicks were positioned onto the channels.

Experimental procedures

The system in Figure S1 was used to carry out two experiments:

1) In the first experiment, aqueous solutions of hydrophilic yellow and hydrophilic blue food dye were applied to the source pads, which were both located on the same side of the central channel. This led to a unidirectional side-by-side flow of the same phase. Next, one of the source pads was switched to the opposite side of the channel. See Figure 1A in the main text.

2) In the next experiment, both source pads were again positioned on the same side of the central channel. One of the pads was soaked with aqueous solution of hydrophilic yellow food dye, the other with octanol containing the hydrophobic blue dye. See Figure 1B in the main text.

The system geometry shown in Figure S2 was used to carry out the following three experiments depicted in Figure 1E-F, Figure 3, and Figure 4, respectively, in the main text:

1) Instead of using one untreated channel and one AKD-coated channel as shown in Figure S2, both channels were untreated in the first experiment in Figure 1E-F. Furthermore, the wetting with water and octanol of the two channels was done before bringing them into contact. After the wetted channels were brought into contact, the source pads and outlet wicks were placed. The source pads contained an aqueous solution of hydrophilic yellow food dye and octanol with hydrophobic blue dye, respectively. See Figure 1E-F in the main text.

2) Now the setup and exact protocol depicted in Figure S2 was used. The source pads contained water with hydrophilic yellow food dye and octanol with hydrophobic blue dye, respectively. See Figure 3 in the main text.

3) The setup and exact protocol depicted in Figure S2 was again used for a demonstration of countercurrent liquid-liquid extraction. The source pads contained pure water and a saturated octanol solution of basic fuchsin, respectively. After the octanol channel was filled with purple basic fuchsin solution, the aqueous pad was replaced with a pad containing 1 M HCl solution. As soon as the fuchsin was extracted from the octanol flow, the aqueous pad was replaced with a pad containing pure water. See Figure 4 in the main text.

Off-Paper Partitioning of the dyes and basic fuchsin

In order to visualize the affinity for different solvents of the dyes used (hydrophilic yellow, hydrophilic blue, hydrophobic blue), two-phase, 1-octanol/water systems were prepared in sealed glass vials. These systems were kept for 24h and shaken regularly. Afterwards, the phases were allowed to separate and images were acquired (Figure S3). A similar experiment was conducted for basic fuchsin. Two mg of basic fuchsin was added to 5 mL of either water, 1 M HCl in water, or 1-octanol. Next, 5 mL of 1-octanol was added to both aqueous solutions separately and shaken to allow partitioning (Figure S4).

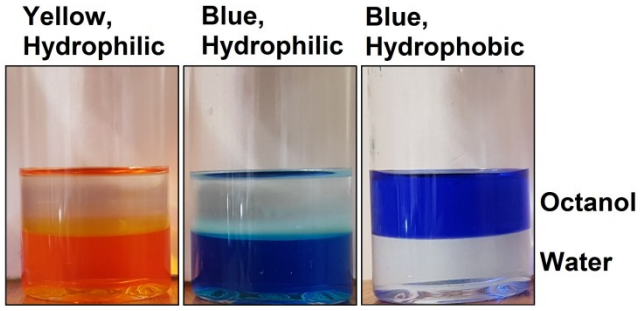

Figure S3. Partitioning of the three dyes used between water and 1-octanol. The dyes are a hydrophilic yellow dye, a hydrophilic blue dye and a hydrophobic blue dye. Clearly, the hydrophilic dyes remain in the aqueous phase, without partitioning substantially into the octanol. The hydrophobic dye, however, behaves in the opposite manner, and occupies the octanol rather than the aqueous phase.

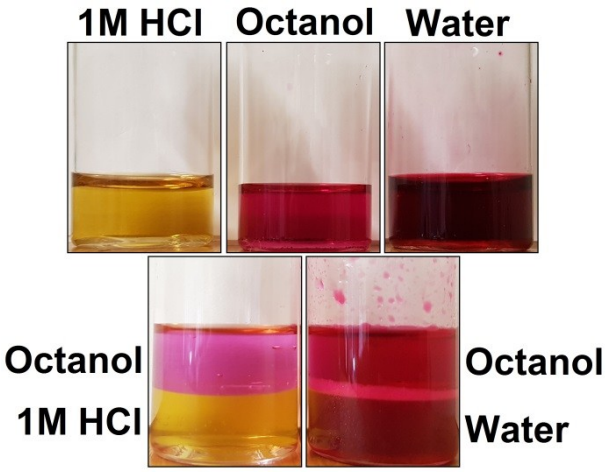

Figure S4. Dissolution of 2 mg of basic fuchsin in 5 mL of either water, 1-octanol, or a solution of 1 M HCl in water, and partitioning of basic fuchsin between octanol and either water or 1 M HCl solution in water. Dissolution in 1 M HCl solution is almost immediate and yields a solution having a light yellow color. Dissolution of basic fuchsin in water and octanol was incomplete after 24 hours, and resulted in dark red and purple solutions, respectively. After adding 5 mL of 1-octanol to the aqueous phases, it is clear that basic fuchsin has a stronger tendency to occupy the acidic aqueous phase than either water or octanol, as evidenced by the difference in color intensities of the respective solutions.

References

[1] X. Li, J. Tian, T. Nguyen, W. Shen, *Anal. Chem.* **2008**, *80*, 9131–9134.