Supplementary Material (ESI) for Lab on a Chip

Surface-directed channels filled with organic solvents

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1. Details of the hypothesis

Consider two parallel glass slides separated by the distance *h*. These slides are flat, and do not have any chemical surface patterns. Although surface-directed channels are normally formed using hydrophilic-hydrophobic surface patterns, the channels described in this paper are different from them in the fact that they utilize chemically homogeneous surfaces. If some liquid (*e.g.*, *m*-xylene) exists between such homogeneous surfaces, it may have a disc shape rather than a long and narrow rectangular shape. Because the liquid-air interface area of the disc shape is smaller than that of the rectangular shape, the disc shape is advantageous from the viewpoint of the total surface energy of the system. However, the rectangular shape can stably exist under certain conditions as described in the following discussion.

Assume that the initial shape of the liquid is the rectangular shape of width *w* and length *L*. It will spontaneously shorten its length to *L*-2*dx*, and expand its width to *w*+2*dy* in order to decrease the liquid-air interface area (Fig. 1). Because the volume of the liquid is constant,

$$wLh = (w + 2dy)(L - 2dx)h. \tag{S1}$$

The surface energy changes by an amount *dE* as,

$$dE = 4wdx(\gamma_{SV}' - \gamma_{LS}) + 4(L - 2dx)dy(\gamma_{LS} - \gamma_{SV}) + \{2(w + 2dy + L - 2dx) - 2(w + L)\}h\gamma_{LV}, \tag{S2}$$

where γ_{SV}, γ_{LS}, and γ_{LV} are the surface energies per unit area at the solid-air, liquid-solid, and liquid-air interfaces, respectively. In addition, γ_{SV}' is used as the energy for the solid surface that underwent wetting because the properties of the solid surface can be changed by such an experience. For example, when the surface has a rough texture, the surface energy at the solid-air interface can be changed by wetting because microscopic valleys on the solid surface retain a small amount of water.

Considering the equilibrium of the forces acting on the three-phase contact line, γ_{SV} and γ_{SV}' are written as,

$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV}\cos\theta, \tag{S3}$$

$$\gamma_{SV}' = \gamma_{LS} + \gamma_{LV}\cos\theta', \tag{S4}$$

where θ and θ' are the contact angles on the longer side (L) and the shorter side (w), respectively. Because dE/dx=0 at equilibrium and $\theta<\theta_A$, $\theta'>\theta_R$, Eqs. S1-S4 becomes,

$$\cos\theta_R - \cos\theta_A > \frac{(L-w)h}{Lw}, \tag{S5}$$

where θ_A and θ_R are the advancing and receding contact angles, respectively.

Thus, if the condition satisfies Eq. S5, the liquid can retain the long and narrow rectangular shape that can be regarded as a straight microfluidic channel filled with the liquid.

2. Example of curved channels

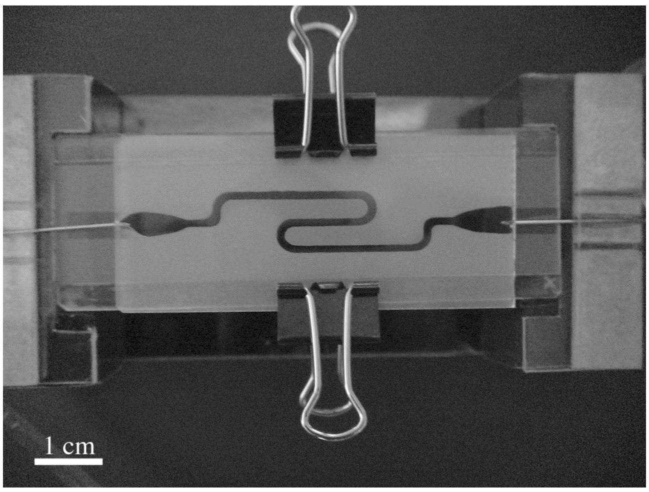

Fig. **S1**. U-shaped channels filled with *m*-xylene. The minimum radius of curvature experimentally achieved was 2 mm.

3. Channels filled with isopentyl acetate and ionic liquid

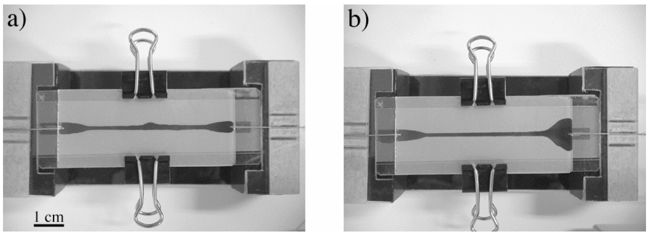

Fig. **S2**. a) The channel was successfully filled with isopentyl acetate, but it was slightly flooded after the fluid flow at 10 μL/min for 5 min. b) Ionic liquid could fill the channel, though continuous flow of this liquid failed.

4. Maximum flow rate without flooding

Assuming laminar flow in a pipe with a circular cross section, the Hagen-Poiseuille equation gives the volume flow rate Q as,

$$Q = \frac{\pi D^4 \Delta P}{128 \eta L}, \tag{S6}$$

where D is the diameter of the pipe, ΔP is the pressure drop ($\Delta P = P_{\mathrm{in}} - P_{\mathrm{out}}$, P_{in} and P_{out} are the pressures at the inlet and outlet, respectively), η is the fluid viscosity, and L is the pipe length.[S1] The average velocity v is,

$$v = \frac{Q}{(D/2)^2 \pi} = \frac{D^2 \Delta P}{32 \eta L}. \tag{S7}$$

When the cross section is not circular, one method for approximating the flow is by replacing D by the hydraulic diameter D_{h} given by,

$$D_{\mathrm{h}} = \frac{4 \times \text{cross section area}}{\text{wetted perimeter}}. \tag{S8}$$

Because the channel used in this study had a rectangular cross section and no sidewalls, the hydraulic diameter can be,[S2]

$$D_{\mathrm{h}} = \frac{4wh}{2w} = 2h. \tag{S9}$$

Replacing D in Eq. S7 by this D_{h}, v is written as,

$$v = \frac{h^2 \Delta P}{8\eta L}. \tag{S10}$$

According to the Laplace equation,[S3] the pressure difference P between in and out of (*i.e.*, the liquid and gas phases of) a long straight channel can be written as,

$$P_{\mathrm{in}} = \gamma_{\mathrm{LV}} \frac{1}{R_1} = -\frac{2\gamma_{\mathrm{LV}} \cos\theta_1}{h}, \tag{S11}$$

$$P_{\mathrm{out}} = \gamma_{\mathrm{LV}} \frac{1}{R_2} = -\frac{2\gamma_{\mathrm{LV}} \cos\theta_2}{h}, \tag{S12}$$

where γ_{LV} is the surface tension of the fluid, R_1 and R_2 are the radii of the side of the channel at the inlet and outlet of the channel, respectively, and θ_1 and θ_2 are the contact angles at these positions (Fig. S3).

The maximum pressure that withstands flooding at the inlet can be obtained by replacing θ_1 by θ_{A} in Eq. S11. Because the fluid in the channel is sucked from the outlet, the pressure of the fluid there can be negative. Therefore, the minimum pressure at the outlet can be obtained by replacing θ_2 by θ_{R} in Eq. S12. The pressure drop, ΔP, between the inlet and outlet should then satisfy

$$\Delta P = P_{\mathrm{in}} - P_{\mathrm{out}} < \frac{2\gamma_{\mathrm{LV}}}{h}(\cos\theta_{\mathrm{R}} - \cos\theta_{\mathrm{A}}), \tag{S13}$$

in order to prevent flooding. Because $Q=whn$, Eqs. S10 and S13 give,

$$Q < \frac{wh^2\gamma_{\mathrm{LV}}}{4\eta L}(\cos\theta_{\mathrm{R}} - \cos\theta_{\mathrm{A}}). \tag{S14}$$

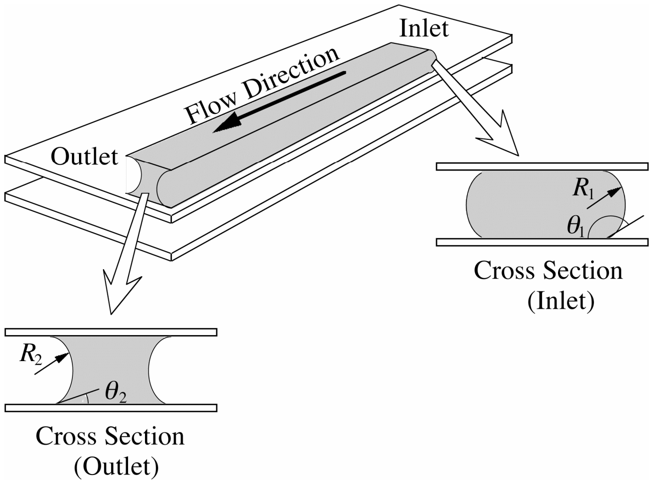

Fig. **S3**. Possible cross sections of the channel at the inlet and outlet of the channel.

5. Maximum flow rates theoretically and experimentally obtained

Table S1. Maximum flow rates that were theoretically and experimentally obtained.

Solvent	Surface tension γ_{LV} (mN/m)	Coefficient of viscosity η (mPa s)	Maximum pressure drop ΔP_{max} (kPa)	Maximum flow rate Q_{max} (μL/min) (Theoretical)[a]	(Experimental)
Water	71.8[Ref. S4]	0.890[Ref. S4]	1.23	712	>99.99
Dimethy sulfoxide	42.9[Ref. S4]	2.00[Ref. S4]	0.508	131	>99.99
Ionic liquid	36.9[Ref. S5]	28[Ref. S6]	0.420	8	–[b]
Nitrobenzene	43.6[Ref. S4]	2.01[Ref. S4]	0.448	115	>99.99
m-Xylene	28.1[Ref. S4]	0.579[Ref. S4]	0.203	180	>99.99
Isopentyl acetate	24.6[Ref. S4]	0.872[Ref. S4]	0.135	80	–[b]

a) Maximum flow rates were calculated using Eq. 4 and the following channel geometry: w=1.0 mm, L=40 mm, and h=0.14 mm.
b) Flow rates could not be measured because of the instability of the channel or the high viscosity of the fluid as described in the Results and Discussion, Section 1.

References

S1. N.-T. Nguyen and S. T. Wereley, *Fundamentals and Applications of Microfluidics, 2nd Ed.*, Artech House, Norwood, MA, USA, 2006, Chap. 2.

S2. B. Zhao, J. S. Moore and D. J. Beebe, *Langmuir*, 2003, **19**, 1873-1879.

S3. P.-G. de Gennes, F. Brochard-Wyart and D. Quere, *Capillarity and Wetting Phenomena*, Springer-Verlag, New York, USA, 2004, Chap. 1.

S4. T. Asahara, N. Tokura, M. Okawara, J. Kumanotani and M. Senoo, *Handbook of Solvents*, Kodansha Scientific, Tokyo, Japan, 1976. (in Japanese)

S5. P. J. Carvalho, M. G. Freire, I. M. Marrucho, A. J. Queimada and J. A. P. Coutinho, *J. Chem., Eng. Data*, 2008, **53**, 1346-1350.

S6. T. Kitazume, T. Fuchigami, H. Sawada and T. Itoh, *Ionic Liquid*, Corona Publishing, Tokyo, Japan, 2005, p. 99. (in Japanese)