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 $L-2dx$, and expand its width to $w+2dy$ in order to decrease the liquid-air interface area (Fig. 1). Because the volume of the liquid is constant,

$$wLh = (w + 2dy)(L - 2dx)h.$$  \hspace{1cm} (S1)

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

$$dE = 4wdx(\gamma_{sv}' - \gamma_{ss}) + 4(L - 2dx)dy(\gamma_{ls} - \gamma_{sv}) + \left\{2(w + 2dy + L - 2dx) - 2(w + L)\right\}h\gamma_{sv},$$  \hspace{1cm} (S2)

where $\gamma_{sv}$, $\gamma_{ls}$, and $\gamma_{sv}$ are the surface energies per unit area at the solid-air, liquid-solid, and liquid-air interfaces, respectively. In addition, $\gamma_{sv}'$ 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, \( \gamma_{SV} \) and \( \gamma_{SV}' \) are written as,

\[
\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos \theta, \quad (S3)
\]
\[
\gamma_{SV}' = \gamma_{LS} + \gamma_{LV} \cos \theta', \quad (S4)
\]

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

\[
\cos \theta_k - \cos \theta_a > \frac{(L-w)h}{Lw}, \quad (S5)
\]

where \( \theta_a \) and \( \theta_k \) 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.](image)
3. Channels filled with isopentyl acetate and ionic liquid

![Fig. S2](image)

**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, \( \Delta P \) is the pressure drop (\( \Delta P = P_{\text{in}} - P_{\text{out}} \), \( P_{\text{in}} \) and \( P_{\text{out}} \) are the pressures at the inlet and outlet, respectively), \( \eta \) 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,

\[
D_h = \frac{4 \times \text{cross section area}}{\text{wetted perimeter}}. \tag{S8}
\]

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

\[ D_h = \frac{4wh}{2w} = 2h. \]  

(S9)

Replacing \( D \) in Eq. S7 by this \( D_h \), \( \nu \) is written as,

\[ \nu = \frac{h^2 \Delta P}{8\eta L}. \]  

(S10)

According to the Laplace equation, 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,

\[ P_{\text{in}} = \gamma_{LV} \frac{1}{R_1} = -\frac{2\gamma_{LV} \cos \theta_1}{h}, \]  

(S11)

\[ P_{\text{out}} = \gamma_{LV} \frac{1}{R_2} = -\frac{2\gamma_{LV} \cos \theta_2}{h}, \]  

(S12)

where \( \gamma_{LV} \) 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 \( \theta_1 \) and \( \theta_2 \) are the contact angles at these positions (Fig. S3).

The maximum pressure that withstands flooding at the inlet can be obtained by replacing \( \theta_1 \) by \( \theta_A \) 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 \( \theta_2 \) by \( \theta_R \) in Eq. S12. The pressure drop, \( \Delta P \), between the inlet and outlet should then satisfy

\[ \Delta P = P_{\text{in}} - P_{\text{out}} < \frac{2\gamma_{LV}}{h} (\cos \theta_1 - \cos \theta_2), \]  

(S13)

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

\[ Q < \frac{wh^2 \gamma_{LV}}{4\eta L} (\cos \theta_2 - \cos \theta_R). \]  

(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.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Surface tension $\gamma_L$ (mN/m)</th>
<th>Coefficient of viscosity $\eta$ (mPa s)</th>
<th>Maximum pressure drop $\Delta P_{\text{max}}$ (kPa)</th>
<th>Maximum flow rate $Q_{\text{max}}$ (µL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>71.8 $^\text{Ref. S4}$</td>
<td>0.890 $^\text{Ref. S4}$</td>
<td>1.23</td>
<td>712</td>
</tr>
<tr>
<td>Dimethy sulfoxide</td>
<td>42.9 $^\text{Ref. S4}$</td>
<td>2.00 $^\text{Ref. S4}$</td>
<td>0.508</td>
<td>131</td>
</tr>
<tr>
<td>Ionic liquid</td>
<td>36.9 $^\text{Ref. S5}$</td>
<td>28 $^\text{Ref. S6}$</td>
<td>0.420</td>
<td>8</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>43.6 $^\text{Ref. S4}$</td>
<td>2.01 $^\text{Ref. S4}$</td>
<td>0.448</td>
<td>115</td>
</tr>
<tr>
<td>$m$-Xylene</td>
<td>28.1 $^\text{Ref. S4}$</td>
<td>0.579 $^\text{Ref. S4}$</td>
<td>0.203</td>
<td>180</td>
</tr>
<tr>
<td>Isopentyl acetate</td>
<td>24.6 $^\text{Ref. S4}$</td>
<td>0.872 $^\text{Ref. S4}$</td>
<td>0.135</td>
<td>80</td>
</tr>
</tbody>
</table>

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


