Gravity-induced reorientation of the interface between two liquids of different densities flowing laminarly through a microchannel

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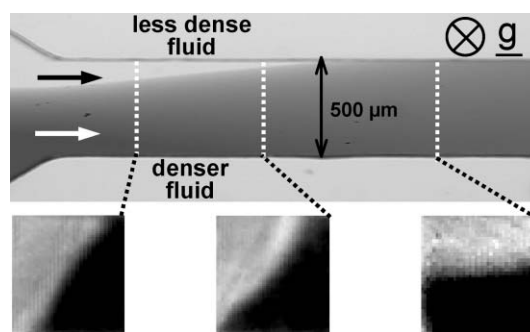
This paper experimentally quantifies the reorientation of the liquid–liquid interface between fluids of different densities flowing side-by-side in pressure-driven laminar flow in microchannels. A gravity-induced pressure mismatch at the interface will gradually drive the denser fluid to occupy the lower portion of the microchannel. The rate of this process is expected to depend on the interplay of viscous forces—which tend to dominate at the microscale—and inertial and gravitational forces. A correlation that relates the position of such a liquid–liquid interface to physical variables and channel dimensions was derived. The extent of reorientation of the streams was then related to two dimensionless numbers: Fr, the square root of the ratio of inertial to gravitational forces; and Re/Fr^2, the ratio of gravitational to viscous forces. Further analysis showed that the reorientation of the streams depends only on the gravitational and viscous forces, but not inertia. The quantitative description of the position of the interface between liquids of different densities described in this paper aids in the rational design of the rapidly growing number of microchemical systems that utilize multistream laminar flow for performing spatially resolved chemistry and biology inside microfluidic channels.

Introduction

Microchemical systems that utilize two or more liquid streams flowing laminarly in parallel in a microfluidic channel have been developed for a wide range of applications. Examples include measurement of analyte concentrations using a "T-sensor";[1] microfabrication of in-channel microelectrodes;[2] etching of relief patterns into the microchannel walls;[3] patterning of channel walls with hydrophilic and hydrophobic paths;[4] patterning of mammalian and microbial cells;[5] liquid–liquid extractions;[6] crystallization of proteins[7] or inorganic salts;[2] studies of protein folding;[8] generation of electrical power using redox flow cells[9] or membraneless fuel cells;[10] and the creation of axisymmetric microscale polymeric structures.[11] These applications all rely on multistream laminar flow, which enables control over local chemical composition within a microchannel. Optimum performance requires understanding and control of the concentration profiles of solutes within these streams. To this end, diffusional mixing at interfaces between pressure-driven laminarly flowing streams, as well as simultaneous diffusion and reaction, have been studied extensively through simulation and experiment in the past decade.[12–14] Similarly, the occurrence of liquid–liquid interfacial instabilities as well as lateral shifting of the liquid–liquid interface have been quantified as a function of the viscosities and volumetric flow rates of the individual streams.[15]

To date, however, reorientation of the vertical liquid–liquid interface between streams of different densities in laminar flow has largely been ignored. Whereas at the macroscale such a vertical liquid–liquid interface would rotate immediately to have the less dense stream flowing on top of the denser stream, the same reorientation process at the microscale is more gradual yet very much present (Fig. 1). Reorientation of the initially vertical liquid–liquid interface to a horizontal position would, for example, obscure optical measurement of the analyte concentration in a T-sensor,[1] lead to loss of patterning fidelity,[2–5] and result in unwanted fuel crossover in membraneless fuel cells.[9,10] Understanding the interplay of forces that dictates the reorientation of fluid streams at the microscale is thus essential to the use and development of microchemical systems based on multistream laminar flow.

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Fig. 1 Optical micrograph (top) and digital camera images of cross sectional views of reorientation of the liquid–liquid interface between two liquids of different densities flowing laminarly in parallel. Dye was added to the denser stream (water). Reorientation is a result of the pressure mismatch at the interface when it is initially parallel to the direction of gravity.

In this paper we experimentally investigated and quantified the reorientation of the liquid–liquid interface between streams of different densities flowing laminarly in a microchannel. We related the extent of reorientation of the streams to two dimensionless numbers: Fr, representing the square root of the ratio of inertial forces to gravitational forces ($Fr = (\rho v^2/hg\Delta\rho)^{1/2}$); and Re/Fr^2 ($Re = \rho vh/\mu$), representing the ratio of gravitational forces to viscous forces.
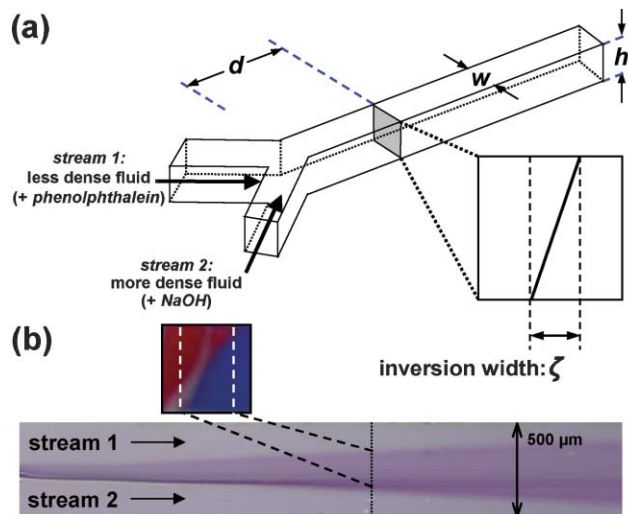
Experimental

Device fabrication

Two methods were used to fabricate the microfluidic channels with square ($250 \times 250\ \mu m^2$ and $500 \times 500\ \mu m^2 = w \times h$) and rectangular ($500 \times 250\ \mu m^2$ and $1000 \times 500\ \mu m^2$) main channel dimensions. The first method used soft lithography.[16] The microchannel was designed using CAD software (Freehand 9, Macromedia) and a high-resolution transparency printed on a high resolution Image Setter (5080 dpi, Herkules) was used as the photomask in contact photolithography to obtain a positive relief structure in photoresist as the master. Then the channel geometry was obtained in polydimethylsiloxane (PDMS) *via* replica molding on a master. The second method to obtain the microreactor channel geometry involved micromachining the desired channel design in polycarbonate sheets (Machine Shop, School of Chemical Sciences, University of Illinois).

After obtaining a substrate (PDMS or polycarbonate) with the desired channel geometry, this PDMS or polycarbonate membrane that carries the Y-shaped microfluidic channel was sandwiched between gasket layers of PDMS. For robustness this three-layer assembly was sandwiched between 1.0 mm thick polycarbonate slabs.

Measurement

The liquid streams were introduced through polyethylene tubing from syringes placed in a syringe pump (Harvard Apparatus, PHD 2000). Water ($\rho = 1000$ kg m^{-3}), ethanol ($\rho = 789$ kg m^{-3}), and mixtures of water and ethanol ($\rho_{mix} = t \times \rho_{water} + (1 - t) \times \rho_{ethanol}$, $0 < t < 1$) were used to obtain streams of different densities. To visualize the orientation of the liquid–liquid interface between the two streams in laminar flow, we utilized the change of the indicator phenolphthalein, present in the less dense stream, from colorless to intense violet in the presence of hydroxide ions, which were present in the denser stream as 0.5 M NaOH (Fig. 2). A Leica MZ12 stereozoom microscope equipped with a Sony CCD video camera was used to capture still images (top view) of the steady-state gradual reorientation of the liquid–liquid interface between the two streams down the channel. Profiles of the violet intensity perpendicular to the direction of flow and at different locations along the channel were obtained from these still images using Scion Image software (Scion, Frederick, MD). The projected width of the interface, defined as the width of the violet intensity region, and from here on referred to as the "inversion width", ζ, was obtained from each captured intensity profile.

Fig. 2 (a) Schematic drawing of the experiment used to visualize (color change upon mixing of NaOH and phenolphthalein) and to quantify (through the inversion width, ζ) the reorientation of the liquid–liquid interface in the microchannel. (b) Optical micrograph (top view) of the reorienting interface between two liquids of different densities (different conditions than in Fig. 1). Inset: cross-sectional view in false color.

The inversion width was measured over the following range of conditions: $v = 0.8$–12 cm s^{-1} (Re varied between 1 and 30), where v is the average fluid velocity; $g\Delta\rho = 0.41$–2.05 kg m^{-2} s^{-2}, where $\Delta\rho$ is the difference in density between the two streams; and $d = 0$–28 mm, where d is the axial distance along the channel. We used the Scion Image software to determine the width of the color intensity peak above 0.5 of the maximum intensity. We assumed that broadening at the interface due to diffusion alone was negligible. To confirm this assumption, we performed a control experiment using two aqueous streams of equal density containing phenolphthalein and sodium hydroxide, respectively. The violet diffusional mixing zone, in this experiment solely due to diffusion, was small relative to the measured inversion widths for all flow rates and devices; always less than 10% of the channel width at the distance where complete reorientation is observed to occur, over the entire range of flow rates used in the reorientation experiments reported here. In all our experiments convection dominates diffusion (*i.e.* medium to high Péclet number systems; $Pe = vh/D$ where D is the diffusion coefficient of one solvent into another), as is the case in most applications that utilize multistream laminar flow. The cross-sectional images in Fig. 1 and 2 were obtained by cutting the PDMS device at several locations perpendicular to the microchannel and then imaging the exiting fluid streams using a digital camera (Nikon Coolpix 4500).

Results and discussion

Relevant physical phenomena

When two streams of different densities converge and share a vertical liquid–liquid interface, a gravity-induced pressure mismatch exists at the interface, rendering the position of the

interface unstable. Due to the high surface-to-volume ratios at the microscale, surface forces such as the viscous force tend to dominate body forces such as inertial and gravitational forces. The liquid–liquid interface only gradually reorients due to the dampening effects of viscous forces on fluid motion. The rate at which reorientation takes place depends on the magnitude of the local pressure mismatch at the interface compared to the viscous and inertial forces within the fluid.

Interfacial tension can also play a role in the reorientation process. In classical theory of capillarity, the interfacial tension between miscible fluids, such as ethanol and water (used here in this work), is nonexistent,[17] and therefore does not affect the reorientation of the interface. For immiscible fluids, however, we would expect that the interfacial tension between the two fluids would slow the reorientation of the interface. The surface area of the fluid–fluid interface is at a minimum value initially, and must increase as the interface reorients. This increase in surface area results in a higher interfacial surface energy and therefore resists the reorientation of the interface. Since most applications that exploit multistream laminar flow use miscible streams, here we limit our analysis to those systems and exclude the analysis of systems with immiscible streams in which interfacial tension is relevant.

Dimensional analysis

To analyze the balance of forces acting on the streams of fluid in laminar flow in microfluidic channels, we developed scaling relationships using dimensional analysis that describe the reorientation of the interface between fluids of different densities. Table 1 lists the five dimensionless groups that we derived using the Buckingham pi theorem, from the following 8 variables: the channel width, w; the channel height, h; the axial distance along the channel, d; the density of the less dense fluid, ρ; the average velocity of the streams, v; a buoyancy constant, $g\Delta\rho$; the average fluid viscosity, μ (here the viscosities of the two streams were similar: $\mu_{water} = 1.00$ cP, $\mu_{ethanol} = 1.07$ cP); and the inversion width, ζ, as defined above.

The dimensionless group π_1 represents the aspect ratio of the channel, h over w, and therefore is fixed by the geometry of the microfluidic channel. π_2 is the ratio of the distance along the channel d to the channel height h and therefore represents a dimensionless distance. π_3 is equal to a modified Froude number Fr, which represents the square root of the ratio of the inertial force ρv^2 to the gravitational force $hg\Delta\rho$. Others have used the latter dimensionless group to characterize the surface wave height between flowing liquids of different density.[18] π_4 is equal to the ratio of the Reynolds number Re to the square of the modified Froude number Fr. The latter dimensionless

group thus represents the ratio of the gravitational force to the viscous force, and therefore does not depend on the inertial force. Also this dimensionless group π_4 has been used previously to characterize the velocity of annular streams of different densities flowing vertically.[19] Finally, the dimensionless group π_5 is the dependent variable and is equal to the ratio of the inversion width ζ to the channel width w. Based on this analysis, the dependent variable π_5 can be expressed as the following:

$$\pi_5 = \pi_5(\pi_1, \pi_2, \pi_3, \pi_4) \tag{1}$$

Experiments and linear regression analysis

First we performed a set of experiments in which the aspect ratio of the channel π_1 was held at a constant value of 1. For this case, π_5 was therefore only a function of π_2, π_3, and π_4. The interface between the two fluid streams was linear for all experiments performed, even as it reoriented (Fig. 1 and 2). Fig. 3 shows plots of $\ln(\pi_5)$ vs. $\ln(\pi_2)$ and $\ln(\pi_5)$ vs. $\ln(\pi_4)$ for both the 250×250 μm^2 and the 500×500 μm^2 channels, and the linearity of these plots indicates that the data are fit by a power law expression. For both devices a line of slope ~ 0.51 was found to fit the experimental data for $\ln(\pi_5)$ vs. $\ln(\pi_2)$. Additionally, data plots of $\ln(\pi_5)$ vs. $\ln(\pi_4)$ were linear with a
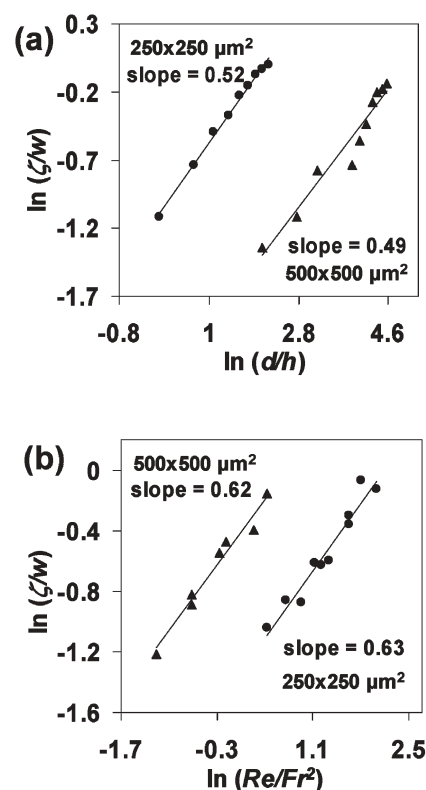
Fig. 3 Log-log plots of the dimensionless inversion width ζ/w: (a) as a function of the length along the channel, $\pi_2(d/h)$, at $\pi_4 = 15.37$ ($\bullet = 250 \times 250$ μm^2 channel) and at $\pi_4 = 1.10$ ($\blacktriangle = 500 \times 500$ μm^2 channel) and (b) as a function of $\pi_4(Re/Fr^2)$ at $\pi_2 = 12$ ($\bullet$) and at $\pi_2 = 48$ ($\blacktriangle$). Lines show the linear regression fits to the data. The inversion width inversely grows as the 0.62 power of π_4 for both channel dimensions.

Table 1 Dimensionless groups for describing the reorientation of the vertical interface between streams of different densities

Dimensionless group	Expression
π_1	h/w
π_2	d/h
π_3	$(\rho v^2/hg\Delta\rho)^{1/2}$ $(=Fr)$
π_4	$h^2 g\Delta\rho/\mu v$ $(=Re/Fr^2)$
π_5	ζ/w

slope of ~ 0.62. A multivariable linear regression was then performed separately on the data collected for both $250 \times 250 \ \mu m^2$ and the $500 \times 500 \ \mu m^2$ channels, resulting in the similar following expression:

$$\pi_5 = 0.075 \pi_2^{0.51} \pi_3^{0.05} \pi_4^{0.62} \quad (2)$$

This power law can be converted to a correlation relating π_5, the inversion width to channel width ratio, with the seven individual variables, with an approximate error of ± 0.05 in the exponents:

$$\pi_5 = \zeta/w = 0.075 h^{0.705} (g\Delta\rho)^{0.595} d^{0.51} \rho^{0.025} v^{-0.57} \mu^{-0.62} \quad (3)$$

One important result of this analysis is that π_5, within experimental error, is independent of π_3 when the other dimensionless groups are fixed. When π_4, the ratio of gravitational forces to viscous forces, is fixed a change in π_3, the square root ratio of the ratio of inertial to gravitational forces, has no effect on inversion behavior. Therefore, the inertial force does not affect reorientation behavior.

In contrast, π_4, the ratio of gravitational forces to viscous forces, does affect the reorientation behavior. As gravitational forces increase relative to viscous forces (increasing π_4), the inversion width increases as expected. As the density difference between the fluids increases, the pressure mismatch is greater and the force driving the reorientation of the interface is greater, leading to a larger inversion width at the same position along the channel. Additionally, as viscous forces are increased relative to gravitational forces, there is greater resistance to fluid reorientation, leading to a smaller inversion width.

We repeated experiments with channels with an aspect ratio of 1 : 2, *i.e.* $\pi_1 = 0.5$. The results show that the dependence of π_5 on π_2, π_3, and π_4 is not affected by the change in π_1 from 1 to 0.5. π_5 was proportional to $\pi_1^{-0.12}$, which resulted in a ~ 9 percent increase in the degree of reorientation of the interface (*i.e.* π_5) when changing the aspect ratio from 1 : 1 to 1 : 2. Although the channel is twice as wide and the interface must shift twice as far horizontally for π_5 to remain constant, the increased distance between the side walls reduces the viscous forces that dampen the reorientation process. The weak dependence, though, of π_5 on π_1 when reducing the aspect ratio from 1 : 1 to 1 : 2 indicates that the channel geometry only weakly affects the interplay of gravitational and viscous forces that determine reorientation behavior.

Conclusions

In sum, we have studied reorientation of the interface between two laminarly flowing streams of different density within a microchannel. We obtained a correlation relating the reorientation of the interface to the viscous, gravitational, and inertial forces, and further analysis showed that the inertial force did not affect the reorientation behavior over the range of experimental conditions. The correlation applies to reorientation of miscible fluids of similar viscosity and equal flow rate within square channels and rectangular channels with an aspect ratio between 1 : 1 and 1 : 2 operated under medium to high Péclet number conditions, as is common for multistream laminar flow applications. For low Péclet number systems, however, diffusion is rapid relative to convection, and diffusional mixing would result in a shallow density gradient rather than a sharp step change in density at the liquid–liquid interface, resulting in a slower reorientation process or complete mixing of the two streams. Reducing the aspect ratio by a factor of two resulted in a modest increase in the degree of reorientation of the interface. The increased distance between the side walls reduces the viscous forces that dampen the reorientation process.

Even though the derived quantitative description for interface reorientation by itself is insufficient to design devices with specific characteristics, the results of this work will provide guidance for rational development of novel microchemical systems that utilize multistream laminar flows comprising fluids of different densities. Along with earlier studies describing scaling laws for diffusional broadening[13] and hydrodynamic spreading of fluids of different viscosities,[15] this paper aids in the optimization and development of novel microchemical systems that utilize multistream laminar flows for performing spatially resolved chemistry and biology inside microfluidic channels.

References

1 B. H. Weigl and P. Yager, *Science*, 1999, **283**, 346–347; A. E. Kamholz, B. H. Weigl, B. A. Finlayson and P. Yager, *Anal. Chem.*, 1999, **71**, 5340–5347.
2 P. J. A. Kenis, R. F. Ismagilov and G. M. Whitesides, *Science*, 1999, **284**, 83–85.
3 S. Takayama, E. Ostuni, X. Qian, J. C. McDonald, X. Jiang, P. LeDuc, M.-H. Wu, D. E. Ingber and G. M. Whitesides, *Adv. Mater.*, 2001, **13**, 570–574.
4 B. Zhao, J. S. Moore and D. J. Beebe, *Science*, 2001, **291**, 1023–1026.
5 S. Takayama, J. C. McDonald, E. Ostuni, M. N. Liang, P. J. A. Kenis, R. F. Ismagilov and G. M. Whitesides, *Proc. Natl. Acad. Sci. USA*, 1999, **96**, 5545–5548; S. Takayama, E. Ostuni, P. LeDuc, K. Naruse, D. E. Ingber and G. M. Whitesides, *Chem. Biol.*, 2003, **10**, 123–130; R. S. Kane, S. Takayama, E. Ostuni, D. E. Ingber and G. M. Whitesides, *Biomaterials*, 2002, **20**, 2363–2376.
6 M. Tokeshi, T. Minagawa, K. Uchiyama, A. Hibara, K. Sato, H. Hisamoto and T. Kitamori, *Anal. Chem.*, 2002, **74**, 1565–1571.
7 B. Zheng, L. S. Roach and R. F. Ismagilov, *J. Am. Chem. Soc.*, 2003, **125**, 11170–11171; B. Zheng, J. D. Tice and R. F. Ismagilov, *Anal. Chem.*, 2004, **76**, 4977–4982.
8 L. Pollack, M. W. Tate, N. C. Darnton, J. B. Knight, S. M. Gruner, W. A. Eaton and R. H. Austin, *Proc. Natl. Acad. Sci. USA*, 1999, **96**, 10115–10117; L. Pollack, M. W. Tate, A. C. Finnefrock, C. Kalidas, S. Trotter, N. C. Darton, L. Lurio, R. H. Austin, C. A. Batt, S. M. Gruner and S. G. J. Mochrie, *Phys. Rev. Lett.*, 2001, **86**, 4962–4965.
9 R. Ferrigno, A. D. Stroock, T. D. Clark, M. Mayer and G. M. Whitesides, *J. Am. Chem. Soc.*, 2002, **124**, 12930–12931.

10 E. R. Choban, P. Waszczuk, L. J. Markoski, A. Wieckowski and P. J. A. Kenis, *Proceedings of the 40th Power Sources Conference*, Cherry Hill, 2002, pp. 317–320; E. R. Choban, L. J. Markoski, A. Wieckowski and P. J. A. Kenis, *J. Power Sources*, 2004, **128**, 54–60; J. L. Cohen, D. A. Westly, A. Pechenik and H. D. Abruña, *J. Power Sources*, 2005, **139**, 96–105; A. Bazylak, D. Sinton and N. Djilali, *J. Power Sources*, 2005, **143**, 57–66.

11 W. Jeong, J. Kim, S. Kim, S. Lee, G. Mensing and D. J. Beebe, *Lab Chip*, 2004, **4**, 576–580.

12 A. E. Kamholz and P. Yager, *Biophys. J.*, 2001, **80**, 155–160.

13 R. F. Ismagilov, A. D. Stroock, P. J. A. Kenis, G. Whitesides and H. A. Stone, *Appl. Phys. Lett.*, 2000, **76**, 2376–2378.

14 A. Hatch, A. E. Kamholz, K. R. Hawkins, M. S. Munson, E. A. Schilling, B. H. Weigl and P. Yager, *Nat. Biotechnol.*, 2001, **19**, 461–465; A. E. Kamholz, E. A. Schilling and P. Yager, *Biophys. J.*, 2001, **80**, 1967–1972.

15 P. J. Stiles and D. F. Fletcher, *Lab Chip*, 2004, **4**, 121–124.

16 D. C. Duffy, J. C. McDonald, O. J. A. Schueller and G. M. Whitesides, *Anal. Chem.*, 1998, **70**, 4974–4984.

17 N. K. Adam, *The Physics and Chemistry of Surfaces*, Dover, New York, 1968.

18 E. Jud, A. Crua and U. R. Blumer, *Nucl. Eng. Des.*, 1995, **153**, 173–181.

19 P. J. Stiles and D. F. Fletcher, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1219–1224.