

# Viscosity-dependent enhancement of fluid resistance in water/glycerol micro fluid segments

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**Abstract** The influence of the formation of micro fluid segments on the fluid resistance was studied in an example of water/glycerol mixture by pressure drop measurements in dependence on the flow rate and viscosity. Therefore, a micro fluidic arrangement consisting of two syringe pumps, a pressure sensor and an injector for segment generation was assembled. It was found that micro fluid segments generate a significant enhancement of flow-induced pressure drop. This enhancement depends on the flow rate as well as on the number of microfluid segments and viscosity. The resulting pressure drop can be described by an empirical equation reconsidering flow rate, viscosity, capillary size and number of segments.

**Keywords** Micro fluid segments · Multiphase flow · Viscosity · Pressure drop · Internal convection

## 1 Introduction

The transport behavior and the fluid resistance of liquids are of particular importance for the micro fluidic systems

used in micro reaction technology. The influence of material and process parameters on pressure drop is a key issue for the applicability of specific micro fluidic arrangements or particular reaction devices.

The dependence of pressure drop on material properties is particularly critical in case of non-homogenous systems. Namely, liquid/liquid multiphase system for chemical applications must be optimized with respect to the materials influence on the transport behavior in microfluidics. The segmented flow principle attracts increasing interest due to their particular transport conditions (Link et al. 2004; Thorsen et al. 2001; Burns and Ramshaw 2001; Nisisako et al. 2002; Taniguchi et al. 2002; Shestopalov et al. 2004; Zheng et al. 2004; Köhler et al. 2004). Well-defined residence times are achieved due to the subdivision of liquid columns into small micro fluid segments by introduction of a separation liquid. The segmented flow principle converts the laminar flow of the homogenous fluid into a plug flow. This effect leads to a narrow residence time distribution. The size and distance of segments are controlled by the geometry of the micro channel devices, by the volume flow rates and viscosities of the liquids (Henkel et al. 2004; Köhler and Kirner 2005).

The advantages of multiphase flow lead to a lot of different applications. Micro fluid segments are applied in analytical and bioanalytical processes (Günther et al. 2004; Yu et al. 2005). They are used for DNA diagnostics by miniaturized polymerase chain reaction (Köhler et al. 1998; Curcio and Roeraade 2003) for cultivation and screening of microorganisms (Martin et al. 2003; Grodrian et al. 2004), for toxicological studies (Funfak et al. 2007) and for chemical synthesis (Hessel and Löwe 2002a, b; Song et al. 2003; Günther et al. 2005).

Recently it was shown that interfacial interactions are strongly influencing the transport behavior and the

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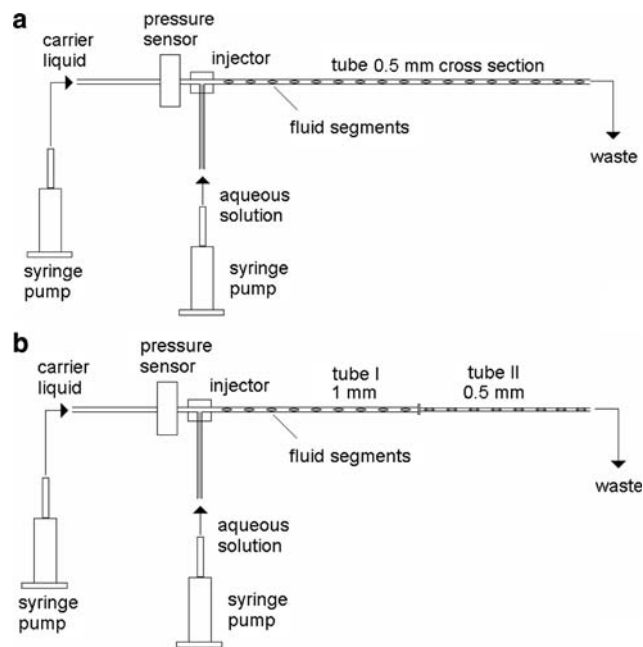
resulting pressure drop in gas/liquid Taylor flow systems (Kreutzer et al. 2005). The shape of the interfaces in streaming segmented fluids depends on the Reynolds number. An excess pressure was found for the transport of segments in liquid/liquid multiphase systems, too (Adzima and Velankar 2006). This excess pressure increases with increasing flow rate and increasing volume fraction of water in a water/hexadecane system. Viscous shear forces and local convection were discussed as reasons for the observed pressure drop. But, investigations on the influence of segment-internal viscosity are still missed in literature to the best of our knowledge.

The existence of liquid/liquid interfaces changes the conditions of convection of segmented flows in comparison with a homogenous laminar flow. The laminar flow is converted into a plug-like transport. This effect must be accompanied by a change in fluid resistance. The dissipation of energy by viscous flow should not only take place in the carrier phase but should also be present in the embedded liquid phase. So, it was expected that the viscosity of segment liquid would have an influence on the pressure drop. Therefore, the influence of segment formation on the change in flow-induced pressure drop for differently composed segments was investigated. Beside flow rates, the influence of the viscosity of segment liquid and the diameter of capillary tube were studied for water/glycerol mixtures embedded in tetradecane as carrier liquid.

## 2 Experimental

Two variants of experimental arrangements were used for the pressure drop measurements. Both were equipped with syringe pumps for the actuation of the carrier liquid (tetradecane) and sample liquid (water or aqueous solution). In both the cases, a pressure sensor was applied in front of the T-type injector, where the formation of the fluid segments occurs.

In the first experimental setup (Fig. 1a), one capillary tube was only applied behind the injector. A PTFE capillary tube with an internal diameter of 0.5 mm was used in the experiments. The pressure sensor allows the monitoring of the pressure drop in the fluid stream between its position and the outlet of the capillary tube. So, the change in pressure drop after switch-on or switch-off of the injected liquid can easily be determined. The recorded pressure is nearly the same as the pressure drop inside the capillary due to the higher fluid resistance of the measurement capillary in comparison with the connector and tube between the pressure sensor and the injector. The arrangement allows the investigation of pressure drop in dependence on volume flow rate, fluid viscosity, segmentation and number of segments.

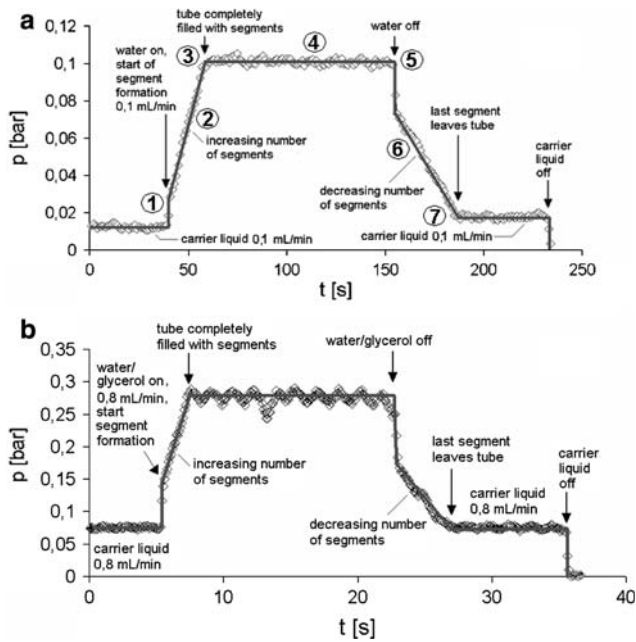


**Fig. 1** Experimental arrangement: **a** segment formation and pressure drop measurement with a single capillary tube with a diameter of 0.5 mm and a length of 120 mm, **b** segment formation and pressure drop measurement with a double capillary set-up with a first tube with a diameter of 1 mm and a length of 180 mm and a second tube with a diameter of 0.5 mm and a length of 120 mm

In the second experimental setup (Fig. 1b), two capillary tubes were arranged one behind the other. The length of the first capillary tube was 180 mm with an internal diameter of 1 mm and that of the second was 120 mm with an internal diameter of 0.5 mm. This arrangement was used for studying the change in segment-induced pressure drop depending on the internal diameter of tubes.

## 3 Results and discussion

The influence of segmentation on pressure drop could be well studied by the single tube arrangement. The effect of segment formation is reflected by the monitoring of pressure signal over time (Fig. 2a, b). The global character of pressure profile is independent of flow rate and liquid composition. But, the specific pressure drop values change. All experiments were performed with a 1:1 ratio of volume flow rates of carrier to sample liquid. The influence of enhancement of the total flow rate after switching on of the aqueous phase is well reflected by the immediate increase of the pressure drop on to the double of the initial value. So the pressure drop was increased from about 15 to 30 mbar when a water flow of 0.1 mL/min in the injector channel was added to a tetradecane flow of 0.1 mL/min (position 1 in Fig. 2a).

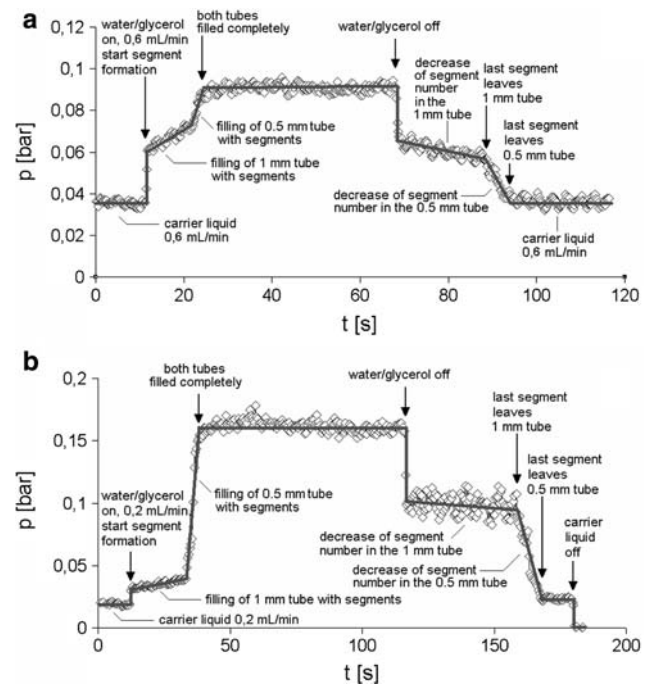


**Fig. 2** Evolution of pressure drop during segment formation and segment release after switch-on and switch-off of segment liquid (aqueous phase) in the single tube arrangement: **a** water as segment liquid, flow rates in both inlet channels: 0.1 mL/min, **b** 60 vol% glycerol, flow rates in both inlet channels: 0.8 mL/min

In contrast to the flow of a homogenous liquid, the pressure increases further during the continuous generation of fluid segments (position 2 in Fig. 2a). This pressure increases continuously as long as the homogenous carrier liquid inside the tube is substituted by fluid segments. It ends when the filling of tube with segments is completed (position 3 in Fig. 2a). Then, the pressure drop in the tube remains constant (position 4 in Fig. 2a). This pressure value is much higher than the expected value for the pressure drop of pure carrier liquid or pure aqueous phase in the tube at the same flow rate.

A certain reduction in pressure drop occurred when the syringe for the aqueous solution was switched off (position 5 in Fig. 2a). The immediate reduction in pressure is much less than half of the total pressure. A further slow pressure reduction corresponds to the loss of fluid segments from the tube (position 6 in Fig. 2a). The time needed for this pressure reduction is the double of that needed for the filling of the tube with segments (between positions 1 and 3) due to the reduction of the total flow rate to half. Finally, the original pressure drop of streaming homogenous carrier liquid was achieved, when the last segment had left the capillary tube (position 7 in Fig. 2a).

The steep increase (jump) in the pressure drop after switch-on of the water flow is due to the increase in total flow rate. At the beginning, there are no segments inside the capillary. The jump in pressure drop is caused by the

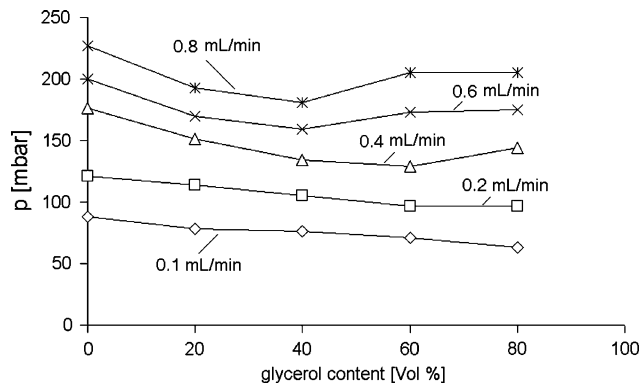


**Fig. 3** Evolution of pressure drop during segment formation and segment release after switch-on and switch-off of segment liquid (aqueous phase) in the double tube arrangement: **a** 20 vol% glycerol as segment liquid, flow rates in both inlet channels: 0.6 mL/min, **b** 90 vol% glycerol, flow rates in both inlet channels: 0.2 mL/min

normal increase of laminar flow. The conditions are different in case of switch-off of water flow. At this time, the capillary is filled with segments. The switch-off of water flow leads to a fast reduction of pressure drop. The amount of this pressure jump is higher than in case of switch-on due to the additional contribution of segments to the total of pressure drop.

The time for filling the tube with segments and the time for the release of the last segment after switching off of the aqueous phase was reduced if the flow rates were enhanced. In addition, an increase in pressure signal was observed. Despite these quantitative features, the character of the temporal pressure profile kept the same (Fig. 2b).

Two phases of pressure increase during the segment formation and two phases of pressure decrease after switching off of aqueous phase were observed if the experimental setup with two capillaries (Fig. 1b) was applied. In principle, the character of pressure profile was analogous to the experiments with the single capillary tube. But, the experiments with double capillary arrangement illustrate well the influence of capillary width and viscosity of aqueous segment phase on the flow behavior (Fig. 3a, b). Here, two experiments with the same order of magnitude of total pressure drop were compared. At lower viscosity (20% glycerol, Fig. 3a), the segment-induced part of pressure drop is nearly the same in both the tubes. The



**Fig. 4** Dependence of pressure drop on glycerol content in aqueous segments for different flow rates, single tube arrangement

segment-induced pressure drop was only a little higher than the pressure drop induced by the flow rate enhancement. This situation is completely changed at higher glycerol content (higher viscosity of aqueous phase, Fig. 3b). Now, the segment-induced pressure drop part was much higher than the pressure drop caused by the flow rate enhancement. In addition, the segment-induced pressure drop in the smaller capillary tube was much higher than the pressure drop in the larger tube. Obviously, the condition of fluid transport in the aqueous phase inside the small tube dominates the total fluidic resistance in this experiment.

The investigation of pressure drop dependence on flow rate and viscosity in the first experimental arrangement showed a significant influence of flow rates, but only a marginal effect of the glycerol content on the pressure drop (Figs. 4, 5). In contradiction to the intuitive expectation, a tendency for slight decrease of fluid resistance with increasing viscosity of water/glycerol mixtures was observed in the flow rate range between 0.2 and 1.6 mL/min (total flow).

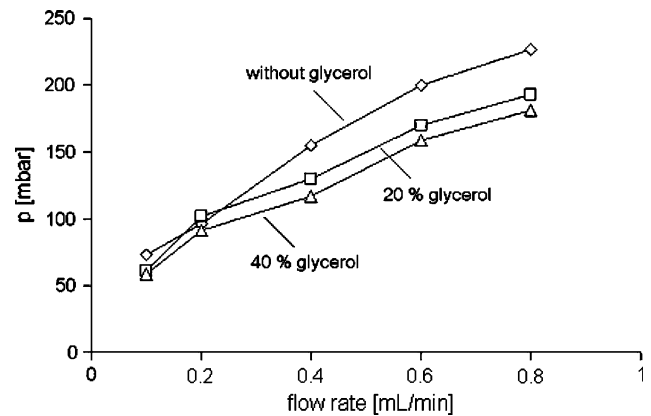
A near linear dependence of the total pressure drop on the reciprocal value of viscosity was found for the water/glycerole mixture of up to 60 vol% glycerol. The parameters for a linear approximated function are dependent on flow rate. This flow rate dependence extrapolated for high viscosities can well be approximated by a square-root function (Fig. 6).

The flow rate and the viscosity dependence in the 0.5-mm capillary tube can be described by an empirical equation reconsidering the measured pressure drops for 0.1, 0.2, 0.4, 0.6 and 0.8 mL/min in each input channel and 0, 20, 40 and 60 vol% glycerol:

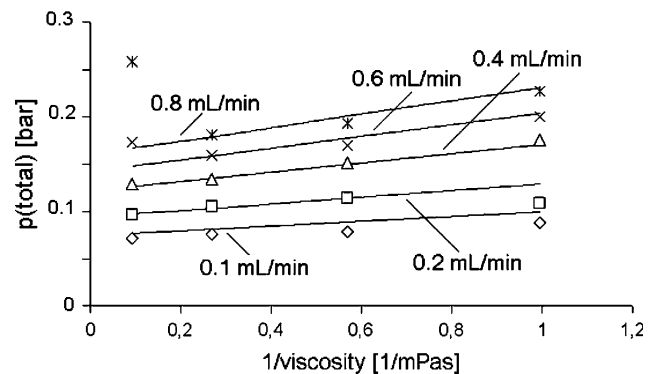
$$p(\text{total}) = a + (b + c/\eta) * \text{sqrt}(\text{flow rate}) \quad (1)$$

with ( $\eta$ , viscosity,  $a$ ,  $b$ ,  $c$  .. empirical parameters:  $a = 27.35 \times 10^{-3}$  bar;  $b = 4.7 \times 10^{-3}$  bar;  $c = 2.5 \times 10^{-11}$  s  $\times$  bar<sup>2</sup>).

The function indicates the general effect of increasing pressure drop on decreasing viscosity in the aqueous phase.



**Fig. 5** Dependence of pressure drop on flow rate in aqueous segments of lower viscosity (pure water, 20 and 40 vol% glycerol, single tube arrangement)



**Fig. 6** Pressure drop—reciprocal viscosity plot for the single tube arrangement (water, 20, 40 and 60 vol% glycerol) for five different flow rates [symbols measurement values, lines calculated functions following Eq. (1)]

In addition, the found relation speaks for a strong viscosity-independent part of the pressure drop. An important part of this pressure drop must be caused by the segmentation-induced convection inside the carrier liquid. It increases with the number of segments inside the capillary and with increasing flow rate. Besides the flow rate dependent part of this pressure drop, there was obtained a flow rate independent part of pressure drop for extrapolations to high viscosity. In our experimental arrangements, this part was about 0.028 bar. If this value is divided by the number of segments inside the capillary, it becomes obvious that this contribution corresponds to the order of magnitude of a capillary pressure. The capillary pressure  $p(\text{cap1})$  for a single interface in the cross sectional area of the tube is given by:

$$p(\text{cap1}) = 2 * \sigma / \text{diameter of tube} \quad (2)$$

for  $d = 0.5$  mm and  $\sigma = 50$  mN/m which must be expected for single interfaces:

$$p(\text{cap1}) = 2 \times 10^{-3} \text{ bar} \tag{3}$$

There is no real capillary pressure due to the symmetry of resident segments. But, the interface conditions are changed between resident segments and segments in motion. The transition between resident and mobile segments results in a change in the shape and size of liquid /liquid interface. The resident segment has a relaxed shape filling the whole channel and possessing a wall contact, whereas a capillary slit of carrier liquid comes between the moving segment and the wall in case of segment motion. This change of interfaces corresponds to an increase in interface energy  $E_{\text{if}(0)}$  which can be regarded as a contribution to the excess pressure of segmented flow. The total energy for a series of segments  $E_{\text{if}(\text{total})}$  should increase with the number of segments:

$$E_{\text{if}(\text{total})} = N \times E_{\text{if}(0)} \tag{4}$$

( $N$ , number of segments)

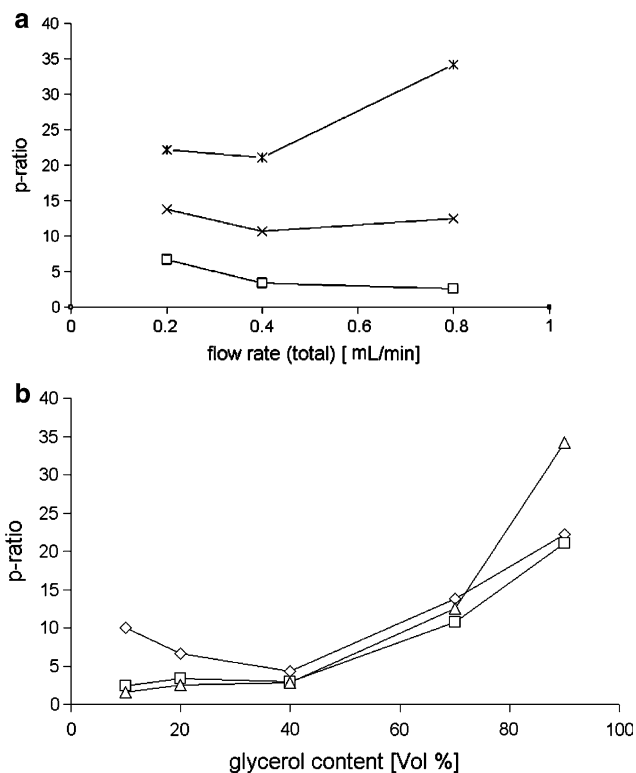
The pressure contribution calculated from pressure drops at extrapolated high viscosities  $p_{\text{if}}$  is obviously in the same order of magnitude as the capillary pressure multiplied by the number of interfaces (example for 7 segments):

$$\begin{aligned} p_{\text{if}} &\approx p(\text{cap, total}) = 2 \times 7 \times 2 \times 10^{-3} \text{ bar} \\ &= 2.8 \times 10^{-2} \text{ bar} \end{aligned} \tag{5}$$

So, it can be concluded that the empirical equation (1) for pressure drop in segmented flow systems can be generalized. The parameter “ $a$ ” can be interpreted as a contribution of interface change between resident and moving segments; “ $b$ ” can be interpreted as mainly influenced by the viscosity and wetting properties of the carrier phase. The parameter “ $c$ ” is mainly determined by the analogous properties of the segment liquid.

The decrease of pressure drop with increasing glycerol content in the aqueous segments can be explained by the enforcement of suppression of segment-internal convection with increasing viscosity. It seems, that the distribution of segmentation-induced convection between two phases with similar viscosity is responsible for a particular high fluid resistance. The change in viscosity ratio between both the liquid phases is accompanied obviously by a certain change in the mechanism of liquid-internal energy dissipation. Differences in the character are probably related to the different interface energies between the liquid phases and the wall, which result in different wetting behavior.

The assumed change in mechanism, which is related to the effect of viscosity increase on flow rate and viscosity dependence of pressure drop, is well reflected by the comparison of the segmentation-induced part of pressure drops in the experiments with two capillary tubes (arrangement of Fig. 1b). The  $p$  ratio is defined by the



**Fig. 7** Effect of flow rate and viscosity of segment liquid on the ratio of segment-induced part of pressure drop (“ $p$  ratio”) in the 0.5-mm and 1-mm-tube: **a** dependence of  $p$  ratio on the flow rate for three water glycerol mixtures, **b** dependence of  $p$  ratio on glycerol content for flow rates of 0.2, 0.4 and 0.8 mL/min

quotient of pressure enhancement due to segments in the 0.5-mm and 1-mm tube. The  $p$  ratio decreases in case of a flow rate increase from 0.4 to 0.8 mL/min at low viscosity (20 vol% glycerol), but increases at high viscosity (90 Vol % glycerol). The change in the  $p$  ratio behavior seems to correspond with the ratio of viscosities of carrier liquid and segment liquid (Fig. 7a). The viscosity of tetradecane at 20 grd C is about 2.18 mPas, 20% glycerol in water shows a viscosity of 1.76 mPas and 40% glycerol 3,76 mPas. The viscosity increases strongly at higher glycerol content and amounts to 22.5 mPas at 70% and 219 mPas at 90% (<http://www.visilex.com> and <http://www.dow.com/glycerine/resources/table18.htm>).

The change in the influence strength of liquids on pressure drop can also be demonstrated by the dependence of the  $p$  ratio (as defined above) on glycerol content (Fig. 7b). The  $p$  ratio remains lower (at higher flow rates) or is decreased (at lower flow rate) if the viscosity of the aqueous phase is similar or lower than the viscosity of the carrier liquid. The  $p$  ratio increases considerably for all flow rates, if the viscosity of the water/glycerol mixture (higher glycerol content) becomes higher than the viscosity of the carrier liquid.

Obviously, the pressure drop in presence of micro fluid segments shows a complex behavior in dependence on flow rate and viscosity. This behavior is caused by the induction of local convection. Instead of a laminar streaming, complex convection pattern arise due to the existence of the liquid/liquid interfaces. The character of the streaming pattern inside the fluid segments and in the segment-separating parts of the liquid column of the carrier liquid is dependent on the viscosity ratio between both the liquids and on shear rates. This effect is illustrated by simulated flow pattern for pure aqueous segments and water/glycerol mixture embedded in tetradecane. The simulations show complex streaming pattern for both the cases. The boundary conditions (no motion in liquid in contact with the walls, equal streaming velocities on both the sides of every point at the liquid/liquid interface) are responsible for the formation of vortices. The existence of such groups of pairwise appearing vortices was proved by  $\mu$ -PIV measurements earlier (Malsch et al. 2008). The simulations show the increase in number of vortices in case of lowering viscosity. The vortices in the tetradecane carrier-fluid are induced by the superposition of the impulse transfer from the channel wall and from the liquid/liquid interface. The vortices inside the segment are induced by the impulse from the tetradecane flow-field between the aqueous segments and from the laminar streaming tetradecane in the slit between segment and tube wall. The higher shear-rates in water ( $\alpha$ ) lead to strong vortices near the liquid/liquid interface and nearly vortex-free central parts. Segments of higher viscosity show enlarged vortices, which are placed in a more central part of the segment.

#### 4 Conclusions

The application of segmented flow leads to a significant increase in fluid resistance in comparison with homogenous streaming liquids. The segmentation-induced pressure drop increases with increasing flow rate and decreasing diameter of the tube. The effect is further increased by the number of fluid segments inside the capillary. The effect of segment formation on fluid resistance was shown clearly by monitoring the evolution of pressure drop after switching on and switching off of the syringe pump for the segment liquid.

It was observed, that the composition of segment liquid has a significant effect on pressure drop. The fluidic behavior of embedded liquid is responsible for an important contribution to the excess pressure in segmented flow. The pressure drop for different flow rates and different viscosities measured with water/glycerol segments in tetradecane was estimated by a general empirical equation. Their parameters were interpreted as total capillary pressure of all segments, and as material-specific coefficients

for carrier and segment liquid. The influence of viscosity ratio on pressure drop speaks for a critical influence of segment-internal convection on the fluid resistance. The observed influence of segment-internal viscosity on excess pressure in micro segmented flow is probably due to the induction of a viscosity-dependent segment-internal liquid motion with strong components perpendicular to the channel axis. The segment-internal convection is driven by a transfer of impulse from the motion of carrier liquid at the liquid/liquid interface into the embedded phase. Vortices are induced and local velocity gradients inside segments are higher than that in the case of a laminar flow in a homogenous liquid in channels of same size. This complex streaming pattern contributes significantly to the enhancement of viscous energy dissipation. As a result, segment liquid contributes to the excess pressure drop also in case of high contact angles to the wall, that means at low or no wall contact.

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#### References

- Adzima BJ, Velankar SS (2006) Pressure drops for droplet flows in microfluidic channels. *J Micromech Microeng* 16:1504
- Burns JR, Ramshaw CC (2001) The intensification of rapid reactions in multiphase systems using slug flow in capillaries. *Lab Chip* 1:10
- Curcio M, Roeraade J (2003) Continuous segmented flow PCR for ultra-high-throughput miniaturized DNA amplification. *Anal Chem* 75:1
- Funfak A, Brösing A, Brand M, Köhler JM (2007) Micro fluid segment technique for screening and development studies on Danio rerio embryos. *Lab Chip* 7:1132
- Grodrian A, Metze J, Henkel T, Martin K, Roth M, Köhler JM (2004) Segmented flow generation by chip reactors for highly parallelized cell cultivation. *Biosens Bioelectron* 19:1421
- Günther A, Hkan SA, Thalmann M, Trachsel F, Jensen KF (2004) Transport and reaction in microscale segmented gas liquid flow. *Lab Chip* 4:278–286
- Günther PM, Möller F, Henkel T, Köhler JM, Groß GA (2005) Formation of monomeric and novolak azo dyes in nanofluid segments by use of a double injector chip reactor. *Chem Eng Technol* 28:520
- Henkel T, Bermig T, Kielpinski M, Grodrian A, Metze J, Köhler JM (2004) Chip modules for generation and manipulation of fluid segments for micro serial flow processes. *Chem Eng J* 101:439–445
- Hessel V, Löwe H (2002a) Mikroverfahrenstechnik: Komponenten - Anlagenkonzeption - Anwenderakzeptanz - Teil 1. *Chemie Ingenieur Technik* 74:17
- Hessel V, Löwe H (2002b) Mikroverfahrenstechnik: Komponenten - Anlagenkonzeption - Anwenderakzeptanz - Teil 2. *Chemie Ingenieur Technik* 74:185
- Köhler JM, Kirner Th (2005) Nanoliter segment formation in micro fluid devices for chemical and biological micro serial flow

- processes in dependence on flow rate and viscosity. *Sens Actuators A* 119:19–27
- Köhler JM, Dillner U, Mokansky A, Poser S, Schulz T (1998) Proc 2nd Internat Conf on Microreaction Technology (New Orleans) 2:241
- Köhler JM, Henkel Th, Grodrian A, Kirner Th, Roth M, Martin K, Metze J (2004) Digital reaction technology by micro segmented flow—components, concepts and applications. *Chem Engn J* 101:201
- Kreutzer MT, Kapteijn F, Moulijn JA, Chr. R. Klein, Heiszwolf JJ (2005) Inertial and interfacial effects on pressure drop of Taylor flow in capillaries. *AIChE J* 51:2428
- Link DR, Anna SL, Weitz DA, Stone HA (2004) Geometrically mediated breakup of drops in microfluidic devices. *Phys Rev Lett* 92:54503
- Malsch D, Kielpinski M, Merthan R, Albvert J, Mayer G, Köhler JM, Süße H, Stahl M, Henkel Th (2008)  $\mu$ PIV-Analysis of Taylor flow in micro channels. *Chem Eng J* 135:S166–S172
- Martin K, Henkel T, Baier V, Grodrian A, Schön T, Roth M, Köhler JM, Metze J (2003) Generation of large numbers of separated microbial populations by cultivation in segmented-flow microdevices. *Lab Chip* 3:202
- Nisisako T, Torii T, Higuchi T (2002) Chemical reactions in microdroplets by electrostatic manipulation of droplets in liquid media. *Lab Chip* 2:19
- Shestopalov I, Tice JD, Ismagilov RF (2004) Multi-step synthesis of nanoparticles performed on millisecond time scale in a microfluidic droplet-based system. *Lab Chip* 4:316
- Song H, Tice JD, Ismagilov RF (2003) A microfluidic system for controlling reaction networks in time. *Angew Chem* 42(7):768–772
- Taniguchi T, Torii T, Higuchi T (2002) Droplet formation in a microchannel network. *Lab Chip* 2:24
- Thorsen T, Roberts RW, Arnold FH, Quake SR (2001) Dynamic pattern formation in a vesicle-generating microfluidic device. *Phys Rev Lett* 86:4263
- Yu H, Kwon JW, Kim ES (2005) Chembio extraction on a chip by nanoliter droplet ejection. *Lab Chip* 5:344
- Zheng B, Tice JD, Ismagilov RF (2004) Formation of droplets of alternating composition in microfluidic channels and applications to indexing of concentrations in droplet-based assays. *Anal Chem* 76:4977. <http://www.dow.com/glycerine/resources/table18.htm>