3rd Micro and Nano Flows Conference
Thessaloniki, Greece, 22-24 August 2011

Liquid-liquid flows in microchannels

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Abstract In this work the flow patterns are investigated during the flow of an ionic liquid and deionized water mixture in a glass microchannel (0.2mm I.D) for two different inlet configurations (T- and Y-junction). The density, viscosity and surface tension of the ionic liquid [C_4mim][NTf_2] are 1420kg/m^3, 0.029Pa·s and 31.92mN/m respectively. The water phase has a density of 1000kg/m^3, a viscosity of 0.001Pa·s and a surface tension of 73,69mN/m. In most of the patterns observed water was the continuous phase with the ionic liquid forming plugs or a mixture of plugs and drops within it. With the Y-junction and at high mixture velocities a separated pattern was observed with the two fluids flowing in parallel along the channel for the middle range of ionic liquid fractions, while water dispersed as drops was found at high ionic liquid fractions. Pressure drop was measured during regular plug flow which revealed that for the same ionic liquid superficial velocity the pressure drop was lower when it flowed in a mixture with water than when it was on its own in the channel. For a constant ionic liquid flow rate, pressure drop decreased as the ionic liquid fraction increased.

Keywords: Micro-fluidics, liquid-liquid, flow patterns, segmented flow

1. Introduction

1.1 Multiphase flows

Multiphase flows (gas-liquid, liquid-liquid) in microchannels have emerged as an important area of research because of their numerous applications in areas such as chemical analysis and synthesis, intensified reactors, micropower generation, fuel cells, thermal management systems, biochemical synthesis. Understanding of the flow characteristics, pressure drop, mass and heat transfer are essential in the design and the precise control of those devices. In the case of two-phase flow in microchannels, the interfacial tension and viscosity forces control the flow patterns while gravity and inertia effects become negligible (Kreutzer et al.,2005). Although there are many studies concerning gas-liquid flows, only limited ones have been reported on the flow behaviour of two immiscible liquids in small channels.

1.2 Liquid-liquid flow patterns in microchannels

In liquid-liquid systems depending on the liquids and the channel material, either phase can wet the channel wall and for phases with similar wettabilities either liquid can intermittently adhere to the wall, rendering ordered, stable and well-defined pattern more difficult to form than in gas-liquid flows Wegmann et al. (2006). Furthermore, the viscosity of both phases must be taken into account. Two-phase liquid flows in large channels are mainly dominated by inertia forces and have been investigated using experimentation together with numerical and theoretical modelling. Microchannels, with characteristic dimensions in the order of tens to hundreds of microns differ from conventional macro-scale systems as far as the dominant forces are concerned. Because of the small characteristic distances, Reynolds numbers are usually low (Re<2000), and laminar flows are established, so that viscous forces dominate over inertial ones. With decreasing length scales, the significance of surface over volume forces is increased, while effects such as wall wettability, wall roughness and flow confinement become important. The geometry of microchannels significantly influences the transport phenomena between phases and thus bends, flow splitters and complicated inlet geometries have been utilized to improve mixing (Shao et al., 2009). The flow patterns appearing in liquid-liquid micro-contactors are influenced by a variety of factors, which can be categorized into 3 groups: (i) channel properties, (ii) fluid properties and (iii) operational conditions Lin and Tavlarides (2009).A large number of investigators have tried to address these factors, in order to gain knowledge of the flow patterns and estimate the area of contact between the fluids. Kashid and Agar (2006) observed that by using fluid mixing zones with different channel inlet diameters, significant changes on slug size and thus interfacial area were obtained during segmented flow. They observed that the capillary microreactor provided very large specific interfacial areas in comparison with other contactors, which enhance mass-transfer rates. Dessimoz et al. (2008) investigated the flow of two immiscible liquids, namely deionised water and dyed toluene or hexane in a rectangular glass microchannel with T- and Y- shaped inlets. The formation mechanisms of slug and parallel flows were studied and the mass transfer performances of the two patterns were compared. The shape of the interface between the immiscible liquids was controlled by a competition between viscous and local interfacial tension forces. Zhao et al. (2006) using oil and water in a PMMA rectangular microchannel identified the following patterns, monodispersed droplets, slug, parallel and annular flow. The formation mechanism of the droplets was further studied in detail.

1.3 Ionic Liquids

One of the common applications involving the flow of two immiscible liquids is extraction which is conventionally carried out using organic solvents. Recently ionic liquids (IL) have been suggested as alternatives to organic solvents because of their negligible volatility and flammability at common industrial conditions, which reduce solvent loss and make them inherently safe and environmentally friendly. Ionic liquids are salts with low melting points while many of them are liquid even at room temperature. In addition, their properties can be tuned by the choice of the anion and cation allowing them to be optimised for a particular application. Hydrophobic ILs are immiscible with water and thus appropriate for liquid-liquid extraction. However, the industrial use of IL has been limited by their high costs (Birdwell et al., 2006). This can be overcome by operating in microchannels which require small solvent hold up. The reduction in solvent volume is compensated by the high efficiencies achieved because of the thin fluidic films formed in the confined spaces of the small channels, which significantly reduce mass transfer resistances. Reactions involving ionic liquids have already been tested in microchannels where much higher yields than in intensely mixed batch processes were found Pohar et al. (2009).

The aim of the present study is to investigate the flow patterns formed and the corresponding pressure drop during the flow of an ionic liquid and water in a microchannel. This is the first time that such a study is presented. Compared to previous flow pattern studies in microchannels, the IL used has greater viscosity than usual organic solvents, which its density is also higher than that of water.

2. Experimental set-up and procedure

2.1 Experimental apparatus

A schematic of the experimental set up used in this study is depicted in Figure 1. It comprises of three main sections: the fluid delivery section in the mixing zone, the flow visualization section and the pressure drop measurement section. An ionic liquid and deionized water were used as test fluids. The ionic liquid was [C_4mim][NTf_2] with initial viscosity μ=0.052Pa·s and saturated with water viscosity of $\mu_{sat.}$=0.029Pa·s and density ρ=1420kg/m^3. The de-ionized water has viscosity and density μ=0.001Pa·s and ρ=1000kg/m^3 respectively. The surface tension of the water phase is σ_{Water}=73.69mN/m, and the surface tension of the saturated ionic liquid is

σ_{IL}=31.92mN/m. Surface tensions were measured with a Kruss contact angle measuring system. The interfacial tension between the two fluids is $\gamma_{Water-IL}$=13.20mN/m as given by Gardas et al. (2010). Two syringe-pumps (Aladdin-1000) were used to feed the liquids to the mixing zone. The uncertainties in the flow rates are estimated to be ±1%. Two inlet configurations (Y- and T-junction) were used for mixing the fluids, both made of PTFE with all the branches having the same ID (0.5mm). In the T-junction the two fluids enter the mixing zone perpendicular with the water injected parallel to the test tube. The angles of the inlets of the Y-junction were 120°. The test section was a glass capillary (0.2mm ID, 100mm length). For the pressure drop measurements, a differential pressure meter Comark C9555 (0-30psi) was used, connected to two pressure ports before and after the microchannel as illustrated in Figure 1. Two side channels (t2 in Figure 1) with a length of 5cm each, are used to connect the main channel with the pressure ports.

The flow visualization section comprises a high-speed camera (Phantom Miro 4) connected to a computer for data storage and a light source. Images were acquired at a distance 80mm downstream the inlet.

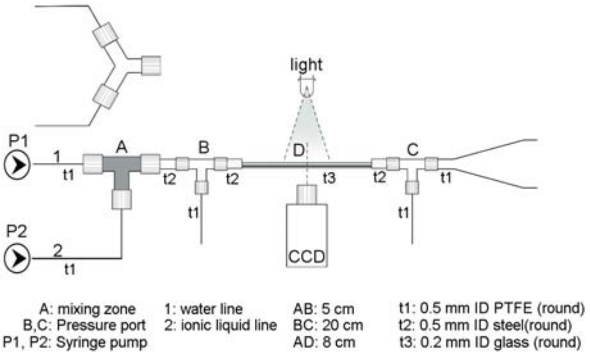

Fig.1. Schematic representation of the experimental apparatus.

2.2 Experimental procedure

Flow patterns were investigated for different flow rates of the two phases. The ionic liquid flow rate varied from 0.065 to 11.31ml/h (which corresponds to superficial velocities of ionic liquid inside the test capillary from 0.058-10cm/s) and that of water from 0.016 to 214.9ml/h (0.014-190cm/s). The Reynolds numbers ($Re=\rho VD/\mu$) for the single phase flow of each liquid ranged for the ionic liquid from 0.003-0.54 (initial IL) and from 0.005-0.97 (saturated IL) and for water from 0.02-377.7. The input ionic liquid volume fraction varied from 0.05 to 0.8.

Initial experiments showed that the patterns were affected by the phase that initially filled the test channel. For that reason experiments were conducted with one of the phases (water) filling the channel initially. In a typical experiment the channel was filled with water first to ensure that water will be the continuous phase. The required flow rate of ionic liquid was chosen and water was injected at the maximum flow rate required for that flow rate of the ionic liquid. The ionic liquid was then introduced at the chosen flow rate. When steady state was reached pressure drop was measured and the flow configuration was recorded. Subsequently, the flow rate of water was decreased stepwise. After a set of experiments was completed, the same procedure was repeated with the next chosen flow rate of ionic liquid. The same experiments were also performed by injecting the water at its minimum flow rate for a particular ionic liquid flow rate and increasing it stepwise. The flow patterns recorded were the same for both procedures.

A few experiments were carried out with the IL filling initially the channel and indicative results will be discussed.

When a set of experiments was completed, the microchannel was cleaned by injecting dichloromethane (Cl_2CH_2) to remove any residual ionic liquid. Air was then injected to dry the channel. This procedure was performed to ensure reproducibility of the experimental conditions.

3. Results and discussion

3.1 Flow patterns

The flow patterns observed with both the T- and Y-inlets will be discussed and tabulated in flow pattern maps. One of the problems in studying and reporting liquid-liquid flow patterns is the lack of coherence in the terminology used by various investigators for the different flow regimes. In this work, the main flow regimes observed are plug flow (also known as segmented flow and in gas-liquid systems as Taylor flow), intermittent flow and “plug and drop train” flow. These can be further divided into regimes that do have mixed characteristics and appear usually at the boundaries of the main patterns.

- T-junction

The flow pattern map obtained with the T-junction can be seen in Fig. 2. The data are presented as the mixture velocity V_{mix} (m/s) in logarithmic scale versus the input of ionic liquid volume fraction ε_{IL}. The lines correspond to the flow patterns observed with the Y-junction.

$$V_{mix} = \frac{Q_{IL} + Q_{water}}{A_{ch}} \tag{2}$$

$$\varepsilon_{IL} = \frac{Q_{IL}}{Q_{IL} + Q_{water}} \tag{3}$$

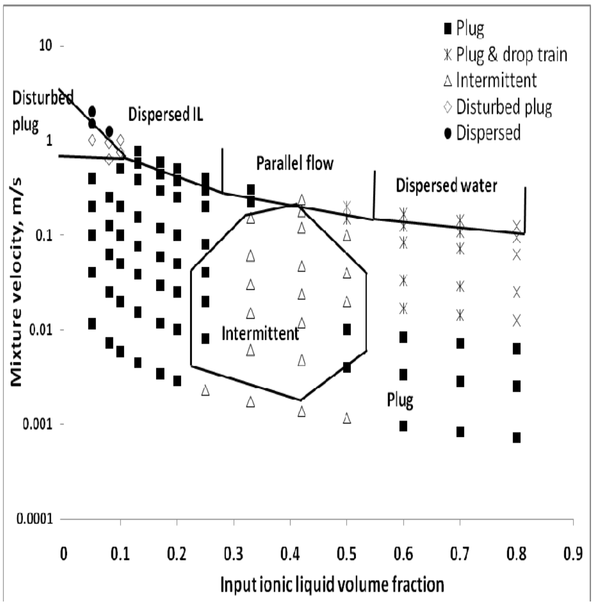

Fig. 2 Flow pattern map for the ionic liquid-water flow in the 0.2mm ID glass microchannel.

In particular:

Plug flow

In this pattern convex shaped plugs of the IL flow are separated by water phase slugs which exhibit a concave geometry. A thin film of water surrounds the ionic liquid plugs. The length of the plugs varied depending on the flow rates conditions. Two kinds of plugs were seen; regular size plugs of 0.3-3mm and elongated plugs whose length varied from 3-30mm. In some cases, in agreement with liquid-liquid flow in larger channels some isolated drops were observed between the plugs.

Examples of these flow patterns are shown in Figures 3 & 4. As can be seen from Figure 2, plug flow occupies a large area of the flow map at low and high ionic liquid fractions. At low $\varepsilon_{IL}<0.25$, plug flow can be observed at the whole range of mixture velocities, apart from $\varepsilon_{IL}<0.1$ and mixture velocities $V_{mix}>0.8$m/s.

At high ionic liquid volume fractions, $\varepsilon_{IL}>0.5$, plug flow was detected only at mixture velocities $V_{mix}<0.01$m/s. In the intermediate fractions, this patterns was only seen for $0.13<\varepsilon_{IL}<0.33$ and high $V_{mix}>0.6$m/s. It should be noted that at high flow rates small disturbances may exist at the front and back of the plug, but as a whole the plug remain intact and uniform.

It was found that the length of the ionic liquid plugs was increasing slightly and that of the water slugs decreasing by decreasing the flow rate of water, while keeping constant the IL flow rate. This size increase was more evident at low mixture velocities, $V_{mix}<0.01$, and ionic liquid volume fraction of $\varepsilon_{IL}>0.6$ where the plug length varied by 5-10%. The same trend was also noticed by increasing the flow rate of ionic liquid and keeping the flow rate of water constant. At high mixture velocities and ionic liquid volume fractions of 0.25-0.42 it seems that by increasing the IL fraction, the plugs retain their length but increase in number due to the rapid penetration of one phase into the other at the inlet, which breaks the IL stream into a greater number of segments. By this way a higher specific interfacial area is achieved that can result in higher mass transfer rates.

Intermittent flow (Plugs with drops at tail)

The intermittent flow regime is characterized by IL plugs with spherical drops of various sizes at their tails (Fig. 4). It is located mainly at mixture velocities $V_{mix}<0.2$m/s and for ionic liquid volume fractions $0.33< \varepsilon_{IL}<0.5$. It is a transition regime between plug flow and "plug and drop train" flow or plug flow with elongated plugs. With increasing mixture velocity the drops at the tails of the plugs became larger. Moreover, at mixture velocities above $V_{mix}>0.04$m/s by increasing the ionic liquid volume fraction the drops at the tails of the plugs increase in size and eventually break up forming smaller ones which spread into the water slug and can even reach the front of the following plug.

Plug and drop train

The term "plug and drop train" is used to describe a flow pattern where ionic liquid plugs of different sizes and drops are flowing together in a row within the water phase, while there is no distinct water slug (Figure 5). This pattern occurred at ionic liquid volume fractions $\varepsilon_{IL}>0.5$. At mixture velocities $V_{mix}>0.01$m/s, as mentioned above, drops at the tails of the ionic liquid plugs appear; as their number is increased with increasing IL fraction they lead to the transition from intermittent to "plug and drop train" flow. It was also observed that by keeping the flow rate of water constant and increasing the flow rate of ionic liquid (water still as the continuous phase) the elongated plugs of the plug flow regime break and form this pattern. An explanation of this could be the low interfacial tension between water and IL which enhance drops to break as seen in Figure 5. It is worth mentioning that in this pattern the ionic liquid would also come in contact with the pipe wall.

Dispersed flow

The dispersed flow (IL in dispersed phase, Figure 6) occurs only at very high mixture velocities $V_{mix}>1$m/s and for low ionic liquid volume fraction $\varepsilon_{IL}<0.08$. It is only seen at these conditions because of the high viscosity of the ionic liquid, which prevents small IL drops to form at higher IL volume fractions. The small Reynolds numbers also contribute to this.

Disturbed plug

The disturbed plug pattern is only detected at high mixture velocities, $0.7\text{m/s}<V_{mix}<1$m/s, and low ionic liquid volume fractions, $\varepsilon_{IL}<0.1$. The high mixture velocity affects the head and the tail of the plugs and waves appear as shown in Figure 7.

When ionic liquid was coming in contact with the tube wall the flow patterns became disturbed. This particularly happened at low mixture velocities. In this case the channel was cleaned and the series of the experiments were repeated. A few experiments were also conducted with the IL injected first in the channel instead of water. It was found that the IL formed a film that covered the microchannel wall and different patterns occurred, for example annular flow with water in the core of the channel as can be seen in Figure 8. It is worth mentioning, that the same annular flow was never found when water was first injected in the microchannel.

- Y-junction

The same patterns were formed when a Y-inlet was used, that occupied similar areas in the flow pattern map (Fig. 2). Intermittent flow was shifted to slightly lower ionic liquid fractions ($\varepsilon_{IL}<0.2$ instead of $\varepsilon_{IL}<0.3$ with T-junction) for the same range of mixture velocities. It is also important to point out that for $\varepsilon_{IL}>0.5$ no "plug and drop train" flow was observed. For the whole range of mixture velocities over this fraction (apart from those where ionic liquid was at its maximum superficial velocity) plug flow was established and at low mixture velocities, $V_{mix}<0.01$, elongated plugs were seen. The IL plugs in the region of $\varepsilon_{IL}<0.5$ at low mixture velocities were slightly bigger in size than those observed with the T-junction. During the intermittent regime, the drops at the plug tails were slightly smaller than those observed with the T-junction. This can be attributed to the reduced mixing of the two liquids in the Y-junction, compared to the

T-junction, which reduces drop break up from the plug tails.

Interestingly, at the highest superficial velocity of ionic liquid and for volume fractions $0.33<\varepsilon_{IL}<0.5$ the two fluids were flowing separated and in parallel to each other. Outside these IL volume fractions and at high mixture velocities the inertia of the ionic liquid-water system was high enough to dominate over surface tension and to form a mixed pattern with IL dispersed for $\varepsilon_{IL}<0.3$ and water dispersed for $\varepsilon_{IL}>0.5$.

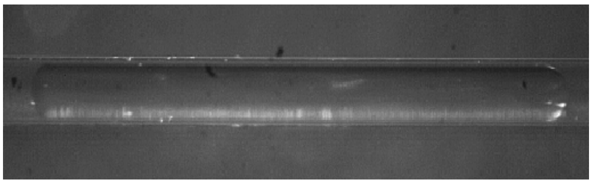

Fig.3. Plug flow

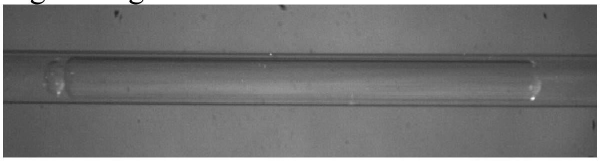

Fig.4. Plug with drops at tail (Intermittent)

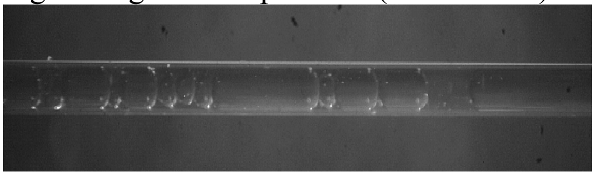

Fig.5. Plug and drop train

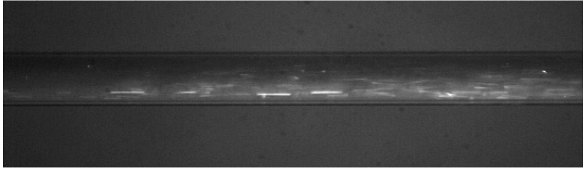

Fig.6. Dispersed flow

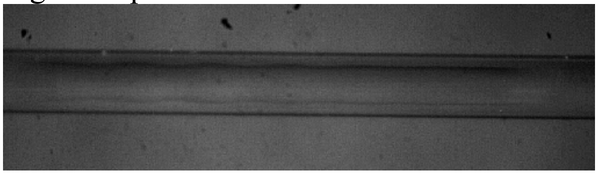

Fig.7. Disturbed plug

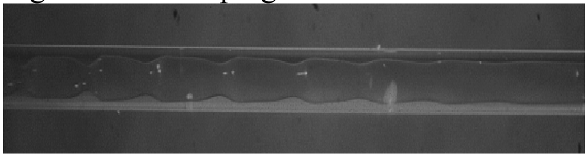

Fig.8. Annular (water in core)

3.2 Pressure drop

In practical sense, knowledge of the pressure drop is required for the prediction and design of an energy efficient system. There are relatively few studies available on pressure drop in liquid-liquid microchannel flows and none that involves ionic liquids. Chakrabarti et al. (2005) at their work investigate the pressure drop characteristics during the simultaneous flow of a kerosene-water mixture through a horizontal pipe for different combinations of superficial velocities.

Initially pressure drop of single phase water was measured along the microchannel at various flow rates and good agreement was found with the Hagen-Poiseuille equation (Eq. 3). Since the viscosity of the IL can change with water intake, single phase experiments with IL saturated with water were taken and the viscosity of the IL was found from the Hagen-Poiseuille equation.

$$\Delta P = \frac{128\mu L Q}{\pi D^4} \qquad (3)$$

During two-phase flow pressure drop was measured for ionic liquid volume fractions of $\varepsilon_{IL}<0.42$ where plug flow is established and where the pressure drop measurements were within the range of the pressure meter. The measurements were repeated 7 times with a repeatability of about 5-10%. The results are shown in Figs. 9 and 10 for the T- and Y-junction respectively against input ionic liquid volume fraction.

The pressure drop of the single-phase laminar flow of ionic liquid ($\varepsilon_{IL}=1$) having the same superficial velocity as the ionic liquid phase in the two-phase mixture was calculated for the various cases using the Hagen-Poiseuille equation and is shown in Figures 9 and 10. It should be mentioned that for the pressure drop measurements the change in diameter from the side channel (0.5mm ID) to the main channel was taken into account.

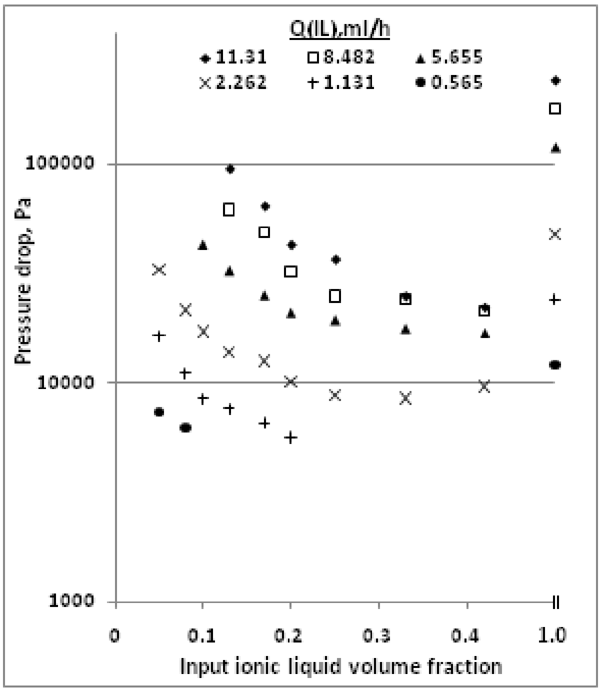

Fig.9. Pressure drop versus input ionic liquid fraction during plug flow at different ionic liquid flow rates for a T- inlet.

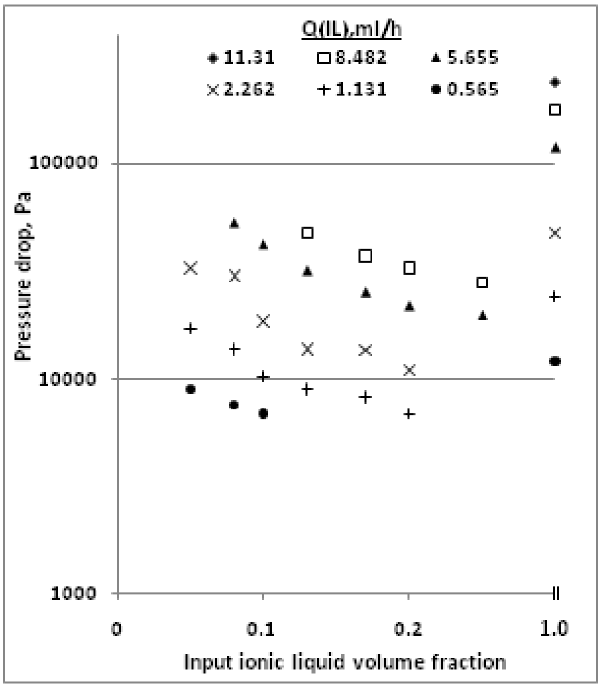

Fig.10. Pressure drop versus input ionic liquid fraction during plug flow at different ionic liquid flow rates for a Y- inlet.

It is very interesting to see that despite the high viscosity of the IL and the high pressure gradient values expected if it were flowing alone in the channel, when flowing in a mixture with water, the pressure drop obtained is much lower. Even the high pressure drops obtained at IL flow rates Q_{IL}>5.655ml/h and at low ε_{IL} are due to the high flow rates and velocities of the water phase and actually approach the single phase water values flowing at the same as the mixture velocities. At lower flow rates it seems that friction forces dominate over velocity forces. These findings are very important because it demonstrates that the high viscosities of the ILs are not limiting factors for their use in small channel flows.

As can be observed from Figure 9, for a constant IL flow rate, the pressure drop is decreased by decreasing the water flow rate (increasing the volume fraction of IL). The same pressure drop measurements were also obtained while decreasing the flow rate of the ionic liquid while keeping the flow rate of water constant. The same trends and similar pressure drop values were found for the Y- inlet (Figure 10).

4. Conclusions

Two-phase ionic liquid - water flow experiments were carried out in a horizontal glass microchannel with 0.2mmID. Flow patterns were investigated for two different inlet configurations, T- and Y- junction. As it was found that the patterns were affected by the phase that initially filled the channel, all experiments were carried out with water as the initial phase.

The main patterns observed were plug flow with the IL in the plugs, intermittent flow with IL drops at the tail of the plug and “plug and drop train” flow where IL plugs and drops were flowing together in a row along the microchannel within water continuous phase. In the case of Y-junction “plug and drop train” flow was not detected, while at the highest mixture velocity and for ionic liquid fractions 0.33-0.5 a separated pattern was seen where the two fluids were flowing side by side. In addition, at high mixture velocities and IL fractions an inversion occurred and water was dispersed into a continuous IL phase.

Pressure drop measurements during plug flow revealed that for the same IL superficial velocity the pressure drop was lower when it flowed in a mixture with water than when it was on its own in the channel. For a constant IL flow rate pressure drop was found to decrease with increasing IL fraction.

5. Acknowledgements

Dr Simon Barrass (UCL) deserves special thanks for his technical advices and invaluable help during the set-up of the experimental apparatus. The project is funded by the Engineering and Physical Sciences Research Council (EPSRC) and the Energy Institute at UCL.

6. Nomenclature

A: cross sectional area, m^2
D: inner diameter of the microchannel, m
L: length of microchannel, m
Q: volumetric flow rate of fluid, m^3/s
Re: Reynolds number
V: superficial velocity, m/s

Greek symbols
ΔP: pressure drop, Pa
ε: volume fraction
μ: dynamic viscosity, kg/m/s
π: constant
ρ: liquid density, kg/s

Subscripts
ch.: channel
IL: ionic liquid
mix.: mixture
sat.: saturated

7. References

Birdwell JF et al. (2006) *Sep. Sci. Technol.*, 41, 2205. [11] Pohar A, Plazl I, Plazl PZ (2009), *Lab Chip*, 9, 3385.

Chakrabarti, D.P., Das, G., Ray, S. 2005. Pressure Drop in liquid-liquid two phase horizontal flow: experiment and prediction. Chem. Eng. Technol., 28, No.9.

Dessimoz, A., Cavin, L., Renken, A., Kiwi-Minsker, L., 2008. Liquid-liquid two-phase flow patterns and mass transfer characteristics in rectangular glass microreactors. Chem. Eng. Sci. 63, 4035-4044.

Gardas, R.L., Ge, R., Ab Manan, N., Rooney, D.W., Hardacre, C. 2010. Interfacial tensions of imidazolium-based ionic liquids with water and n-alkanes. Fluid phase equilibria, 294, 139-147.

Kandlikar, S.G., Grande, W.J. 2003. Evolution of microchannel flow passages- Thermo Hydraulic performance and fabrication technology. Heat Transf. Eng. 24(1), 3-17.

Kashid, M. N., Agar, D. W. 2006. Hydrodynamics of liquid-liquid slug flow: flow regimes, slug size and pressure drop. Chem. Eng. J. 131 (1-3), 1.

Kreutzer, M.T., Kapteijn, F., Moulijin, J.A., Heiszwolf, J.J., 2005. Multiphase monolith reactors: chemical reaction engineering of segmented flow in microchannels. Chemical Engineering Research and Desing 84, 1-7.

Lin, R., Tavlarides, L.L, 2009. Flow patterns of n-hexadecane-CO_2 liquid-liquid two-phase flow in vertical pipes under high pressure. Int. J. Multiphase Flow 30, 225-236

Pohar, A., Plazl, I., Plazl P.Z. 2009. Lipase-catalyzed synthesis of isoamyl acetate in an ionic liquid/n-heptane two-phase system at the microreactor scale. *Lab Chip*, 9, 3385.

Shao, N., Gavriilidis, A., Angeli, P., 2009. Flow regimes for adiabatic gas–liquid flow in micro-channels. Chem Eng Sci 64 (11), 2749-2761.

Wegmann, A., Rudolf von Rohr, P., 2006. Two phase liquid-liquid flows in pipes of small diameters. Int. J. Multiphase Flow 32, 1017-1028.

Zhao, Y., Chen, G., Yuan, Q., 2006. Liquid-liquid two-phase flow patterns in a rectangular microchannel. AlChE Journal, Vol. 52, No. 12.