Application of Double Emulsions based on Paramagnetic Ionic Liquids

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Introduction

Ionic liquids (IL) in general are known for their tuneable properties due to their structural diversity. They consist of a cation core molecule e.g. imidazolium or guanidinium based, and a coordinated anion, mainly halides, BF_4^-, PF_6^-, tosylates or triflates. With suitable complex anions paramagnetic properties can be achieved (MIL), an additional functionality of a pure liquid.
Compared to ferrofluids or other types of nanostructured dispersions, the magnetic response of ionic liquids to external magnetic fields is low, and therefore long-range interactions with an external magnetic field are very weak. Only in a close proximity of a magnet surface a significant responses of the MIL can be observed. Without any doubt, this outstanding property opens up new and unusual possibilities for microfluidic application.[1-4] MILs were used to generate micro double emulsions, thereby gaining selective controlling of the multiphase flow. Emulsion drops could be selectively manipulated in one or two dimensions through external magnetic fields. Different patterns of applied magnetic fields cause different behaviours of the droplets, such as capture and release, coalescence, rotation and distortion, mixing, sorting and phase separation in continuous flow.[5]
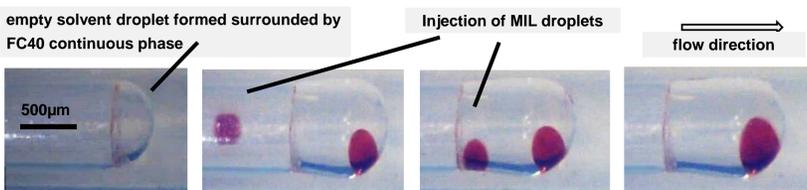
Double Emulsion Processing Unit

- Constructed as a modular capillary microreactor consisting of two commercial available stainless steel T-junctions (Valco). These two T-junctions are connected together in a straight direction by a PTFE-capillary with 150 µm inner diameter (left).
A reproducible flow of alternating organic and paramagnetic ionic liquid slugs is generated. By adjusting the flow parameter a desired volume- or stoichiometric ratio could be achieved.

- At the outlet an additional PTFE-tube with a much wider inner diameter (1000 µm) is mounted at around the outlet of the second T-junction to establish a coaxial capillary-in-tube flow system. By feeding a perfluorinated solvent (FC40) as the continuous phase into the outer tube, regular droplets of a double emulsion are formed (right).
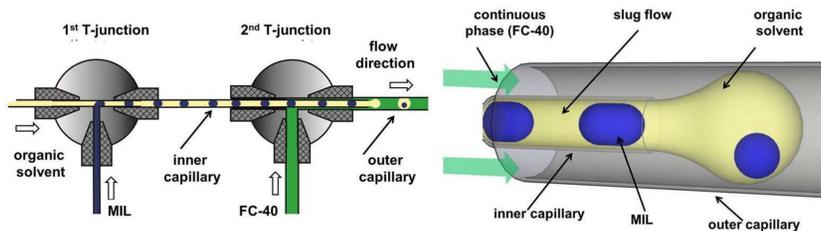
- An organic solvent droplet (toluene) adherent at the capillary-in-tube interface is subsequently filled with $[bmim]_5Dy(SCN)_8$ MIL. The ratio of organic phase and MIL slugs define the amount of MIL in a single double emulsion droplet, while the final emulsion droplet size is mainly determined by the capillary diameter and the flow velocity of the continuous phase. (video clips available at http://www.holger-loewe.de/html/vids.html)

empty solvent droplet formed surrounded by FC40 continuous phase
Injection of MIL droplets
flow direction
500µm

Magnetic Field Simulation

The set of Maxwell equations in SI units describing the magnetic field is :

$$div\vec{B} = 0 \qquad rot\vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad div\vec{D} = \rho \qquad rot\vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{J}$$

For magneto-statics the Maxwell equations can be reduced to

$$div\vec{B} = 0 \qquad rot\vec{H} = 0$$

For each conservative vector field, the scalar potential exists: $\vec{H} = -gradV_m$

It follows: $div\vec{B}(\vec{H}) = div[\mu_0(\vec{H} + \vec{M}(\vec{H}))]$

$$div\vec{B}(\vec{H}) = div[-\mu_0 gradV_m + \mu_0\vec{M}(\vec{H})] - div[\mu_0 gradV_m - \mu_0\vec{M}(\vec{H})] = 0$$

With the relation: $\vec{M} = \chi\vec{H}$

$$-div[\mu_0 gradV_m - \mu_0\vec{M}(\vec{H})] = -div[\mu_0 gradV_m + \mu_0\chi gradV_m]$$
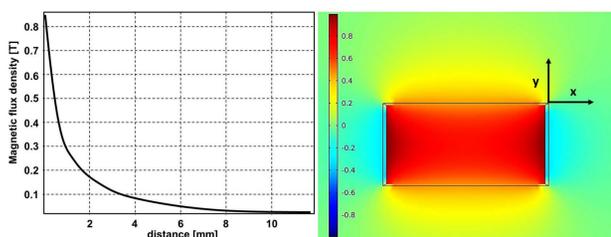$$-div[\mu_0(1+\chi)gradV_m] = -div[\mu_0\mu_r gradV_m]$$
$$-div[\mu_0\mu_r gradV_m] = 0$$

The value for the relative permeability was calculated:

$$\mu_r = \frac{B_r}{\mu_0 H_c} = 1.22NA^{-2}; \quad B_r = 1.47T; \quad H_c = 955kAm^{-1}$$

As a boundary condition the Neumann variant was used:

$$<grad(V_m(\vec{x})),\vec{n}(\vec{x})> = f(\vec{x}), \vec{x} \in \partial\Omega \text{ and } <\frac{\vec{A}}{\|\vec{A}\|},\vec{n}> = 1$$

B: magnetic flux density,
H: magnetic field strength,
D: electric displacement field,
J: current density,
M: magnetization
ρ: charge density
μ_0: permeability of vacuum
μ_r: relative permeability
χ: susceptibility,
V_m: magnetic scalar potential
B_r: remanent flux density;
H_c: coercive field strength
f: normal component of magnetic field strength at the edge $\partial\Omega$ of the magnet,
$\vec{n}$: normal vector on the surface of the magnet.
$\vec{A}$: spatial vector.

The graph shows the modulus of the magnetic flux density normal to the edge. As expected, the magnetic flux decreases exponentially with the distance from the magnets surface. Therefore, magnetic fluid handling seems to be preferred in the micro-scale only. (Magnetic fields were calculated with COMSOL Multiphysics®.)

Capture, Mix and Release

flow direction
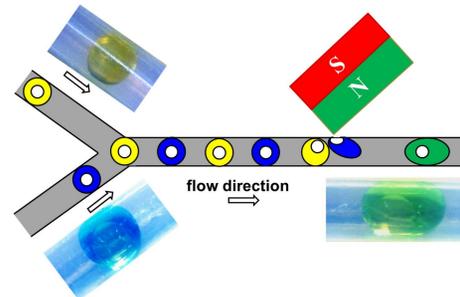
A blue colorized (organic phase) double emulsion droplet with colorless $[bmim]_2MnCl_4$ is captured by a magnet. As subsequent flowing second MIL containing droplet with a yellow colorized organic phase (due to the illumination by the microscope light it appears greenish) is also captured. Bothe organic phases penetrate each other and mix to form a green one. By removing the magnet the now unified green droplet is released.

Shaking and Turning

flow
deformation
rotation
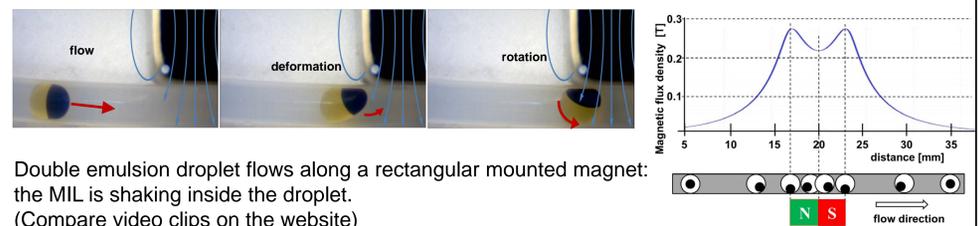
Double emulsion droplet flows along a rectangular mounted magnet: the MIL is shaking inside the droplet.
(Compare video clips on the website)

Separation and Reunification

flow
interaction / acceleration
phase splitting
phase splitting
reunification
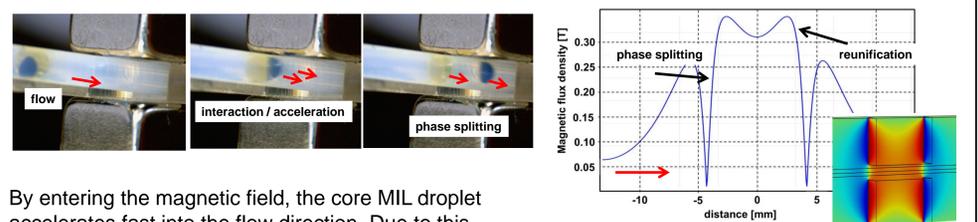
By entering the magnetic field, the core MIL droplet accelerates fast into the flow direction. Due to this speeding up, the MIL droplet separates from the organic phase and the separated organic phase droplet flows afterwards with the continuous phase velocity. This separation is reversible when the MIL droplet reaches a position at the end of the magnets: the flow of the MIL slows down and, at least, the MIL is fixed by the magnetic force until it is reunified with the organic phase droplet. Both, the organic and the MIL phases, appear as the same double emulsion droplet as it enters the magnetic field

Phase Separation

capillary
ring magnet
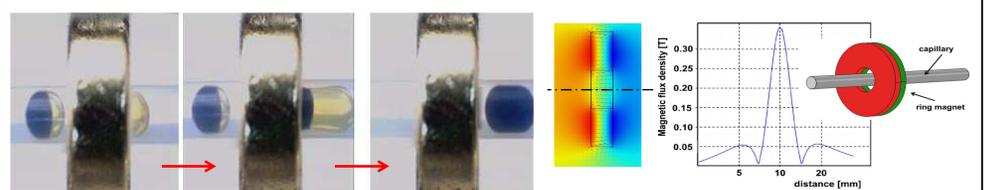
The magnetic flux maximum is in the centre of a ring magnet's hole, the double-emulsion droplets linger at this position and coalescence of a series of droplets occurs. This happens until the cross section of the channel is filled with the grown two-phase composite. A phase separation takes place due to the fixation of the MIL by the magnetic field, i.e. the MIL droplet is stored inside the ring but the organic phase is swept away by the continuous phase flow. Finally, the MIL is partly excerpted by the organic phase droplet due to the surface tension, and pushed out by the arrival of a subsequently following droplet

Summary

Fixation, movement, coalescence and split of MIL containing double emulsion droplets are possible. With arrays of permanent magnets along the flow direction, the inner MIL droplet induces mixing independent from the Reynolds number. The movement of the liquid MIL (instead of solid nanoparticles) for mixing inside of a droplet is surely advantageous for processing of shear force sensitive substances or bio materials. A complete and fast phase separation can be provided even in a continuous flow set up. Furthermore, an easy transfer into chip-sized flow systems is possible.

References

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