

SELF-PROPELLED CHEMOTACTIC DROPLETS

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ABSTRACT

Here we report the chemotactic behaviour of self-propelled ionic liquid droplets on aqueous solutions. These droplets were guided to specific destinations within open channels through the use of chemoattractants such as sodium chloride (NaCl) or hydrochloric acid (HCl). The chemotactic movement of these droplets can be explained by surface tension gradients due to asymmetric release of surfactant from the droplet to the aqueous solution.

KEYWORDS: Micro-Fluidics, Self-propelled, Chemotactic, Droplets, Micro-vehicles

INTRODUCTION

The ability to move in response to an external stimulus is essential for many lifeforms. Certain cells such as bacteria, somatic cells, and other single cell or multicellular organisms move in response to chemical stimuli present in their environment. This phenomenon, known as chemotaxis, is crucial for many biological processes. Notably there are only few equivalents of similar chemotactic-driven “micro-vehicles” in the synthetic world [1]. Using this approach, biomimetic droplets in principle could be moved in a spontaneous manner to desired destinations. This would be particularly useful in the field of microfluidics as an energy-free fluid handling technology.

In this context, surfactants may be employed to control the surface tension of an aqueous-air interface in order to generate unidirectional movement of droplets at the aqueous-air interface. These surfactants can either be dissolved within the aqueous phase [2, 3] or contained within the droplet [1]. Herein, we report for the first time, the spontaneous chemotactic movement of an ionic liquid (IL) droplet at the aqueous-air interface. These single component droplets are self-propelling and can be guided to specific destinations in open fluidic channels through the use of chemo-attractants such as NaCl or HCl.

EXPERIMENTAL

Three different methods of generating the chemical gradients needed for chemotactic propulsion were employed. In the first method the channels were initially filled with a solution of 10^{-2} M NaOH followed by the addition of three to five drops of 10^{-2} M HCl at the desired destination. For the second method the channels were again initially filled with a solution of 10^{-2} M NaOH but this time a hydrogel previously soaked in 10^{-2} M HCl was placed at the desired destination. In the third approach the channels were initially filled with a solution of 10^{-5} M NaCl followed by the addition of few NaCl crystals (~ 10 mg) at the desired destination. In each case, a small droplet of trihexyl(tetradecyl)phosphonium chloride ($[P_{6,6,6,14}][Cl]$) was placed at the starting position 10 – 30 s after addition of the chemo-attractant.

Fabrication of the channels used in this study was carried out using the program AutoCAD 2014 to design the microfluidic platform. A CO₂ laser ablation system (Optec Laser Micro-machining Systems, Belgium) was then used to cut the structures from a 1.1 mm polymethylmethacrylate (PMMA) sheet which had a 50 μ m double sided pressure sensitive adhesive layer, (PSA)(AR8890, Adhesives Research, Ireland) attached. Once cut, the protective layer from the PSA was removed and then the PMMA/PSA layer was laminated with another 1.1 mm PMMA sheet. The final channels were 2 mm wide and 1.1 mm high.

RESULTS AND DISCUSSION

The chemotactic droplets presented here consist of the ionic liquid $[P_{6,6,6,14}][Cl]$ and a small amount of 1-(methylamino)anthraquinone red dye for better visualization. These droplets are designed to move in an open fluidic channel to desired destination through the use of chemoattractants such as HCl and NaCl. The motion of these discrete droplets is controlled by the triggered release of the $[P_{6,6,6,14}]^+$, a very

efficient cationic surfactant, which is a constituent of the IL droplet (Figure 1). The rate of $[P_{6,6,6,14}]^+$ release depends on the concentration of the chloride in the aqueous solution, as the formation of free $[P_{6,6,6,14}]^+$ (the active surfactant at the air-aqueous interface) through dissociation of the relatively closely associated $[P_{6,6,6,14}][Cl]$ ions in the IL depends on the local Cl^- concentration at the IL-aqueous boundary [4]. In the presence of a Cl^- gradient in the aqueous phase, an asymmetrical surface tension gradient is created, leading to a marangoni like flow, which causes the droplet to move from areas of low surface tension towards areas of high surface tension (Figure 2). Chloride gradients were created as described in the experimental section. When such chloride gradients are formed, the $[P_{6,6,6,14}][Cl]$ droplet placed in regions of low Cl^- concentrations (starting position), shows unidirectional movement towards the highest Cl^- concentration (destination), due to the asymmetric release of $[P_{6,6,6,14}]^+$ from the IL droplet into the aqueous phase.

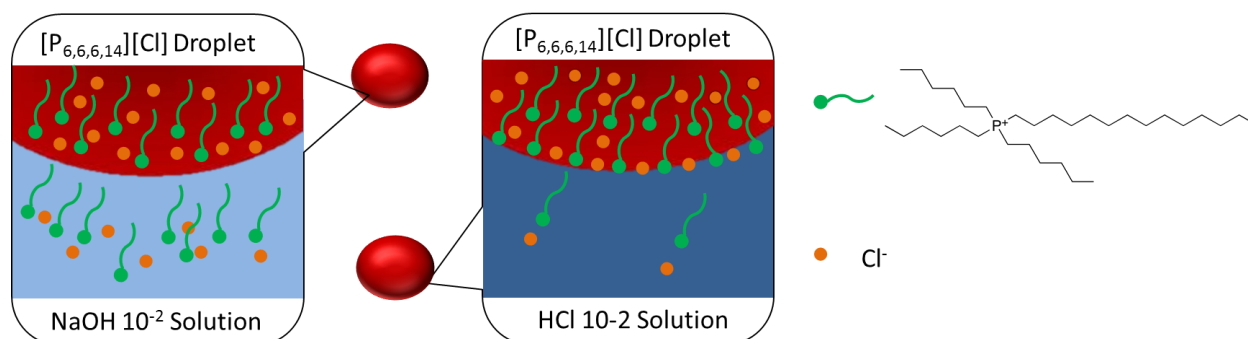


Figure 1: Diagram showing the composition of the $[P_{6,6,6,14}][Cl]$ droplet and the relative solubility of the $[P_{6,6,6,14}]^+$ surfactant in $NaOH\ 10^{-2}\ M$ (left) and $HCl\ 10^{-2}\ M$ (right) solutions.

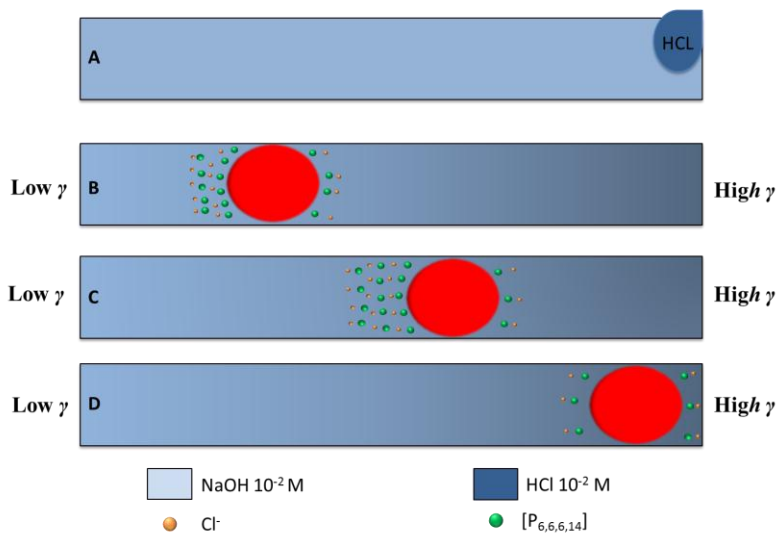


Figure 2: Schematic representation showing the movement of the ionic liquid droplet in open fluidic channels. A - Depicts the preparation of the chloride gradient. The channel was initially filled with $NaOH\ 10^{-2}\ M$ solution. Then at the desired destination two to three drops of $HCl\ 10^{-2}\ M$ solution were added. B - After the formation of the gradient, the IL droplet was placed at the $NaOH$ end of the channel causing surfactant to diffuse into the solution, thus breaking the surface tension symmetry around the droplet. C - Droplet is propelled towards the area of highest surface tension. D - Droplet arrives at the desired destination.

Using this principle, multiple droplet manipulation was also achieved. When multiple droplets were placed at various locations in the channel array at similar times, they would concurrently migrate toward the source of chemoattractant. It was observed that upon arrival at the destination, droplets would often merge to form a bigger droplet (Figure 3).

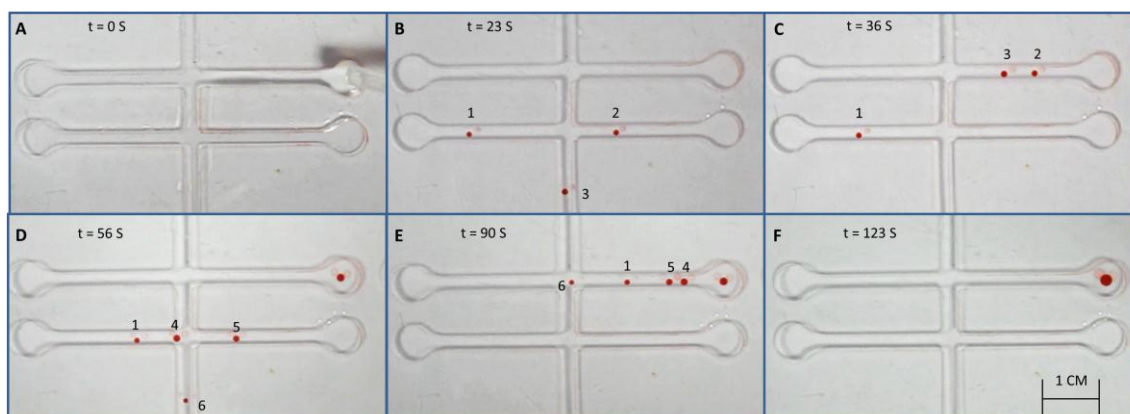


Figure 3: Sequence of snapshots showing multiple droplets moving towards the location where the chemoattractant was introduced. A – Placement of chemoattractant. B – Placement of first three droplets. C – First two droplets moving towards destination. D – Placement of next three droplets. E – Movement of all droplets towards chemoattractant. F – All droplets arrived at destination and merged.

CONCLUSION

In conclusion we have reported the chemotactic self-propelling movement of simple single component IL droplets. These droplets moved without any external energy input and found their way to desired destinations within open-fluidic channels through the use of chemoattractants. It is envisioned that these droplets could be used for dynamic sensing, energy-free micro-cargo transport and as micro-vessels for chemical reactions at pre-determined locations.

ACKNOWLEDGEMENTS

This work was completed under Science foundation Ireland, under the Insight initiative, grant SFI/12/RC/2289.

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