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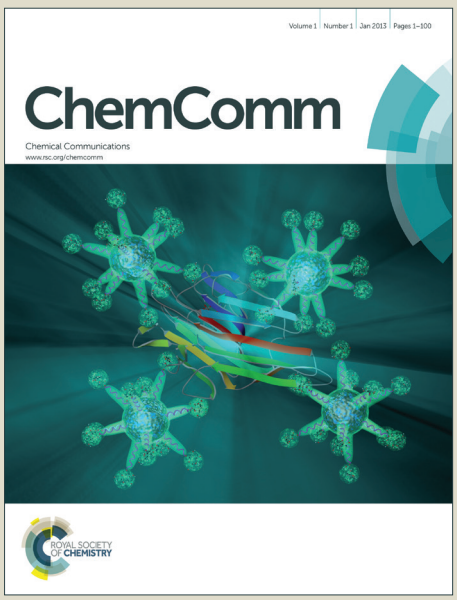

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Self-Propelled Chemotactic Ionic Liquid Droplets

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Herein we report the chemotactic behaviour of self-propelled droplets composed solely of the ionic liquid trihexyl(tetradecyl)phosphonium chloride ($[P_{6,6,6,14}][Cl]$). These droplets spontaneously move along an aqueous-air boundary in the direction of chloride gradients to specific destinations due to asymmetric release of $[P_{6,6,6,14}]^+$ cationic surfactant from the droplet into the aqueous phase.

The ability to move in response to an external stimulus is essential for many life forms. Certain cells such as bacteria, somatic cells, and other single cell or multicellular organisms move in response to chemical stimuli present within their surrounding environment.[1, 2] This phenomenon is known as chemotaxis and it is crucial for many biological processes such as feeding or fleeing toxins, migration and action of somatic cells such as those involved in the immune system,[3, 4] reproductive cells[5] and enzymes.[6] Notably there are only few equivalents of similar chemotactic-driven "micro-vehicles" in the synthetic world. Inspired by chemotactic organisms we developed synthetic biomimetic droplets which are self-propelled and capable of navigating a microfluidic network by introducing chemoattractants at the target destination within the fluidic channel.

Various mechanisms to initiate and direct the movement of micro droplets have been reported, including switchable wettability of a substrate surface via chemical[7, 8] or electro-chemical stimuli,[9, 10] or using temperature gradients,[11, 12] magnetic[13] or acoustic forces[14] and even photo-stimulation to actuate droplets.[15] However, all of these methods involve relatively complex experimental arrangements and/or multi-component droplets, and require applied external energy to create droplet movement.

Surfactant release has been employed to control the surface tension of aqueous systems in order to generate spontaneous movement of droplets at the aqueous-air interface in a contactless manner. When placed into an aqueous system the surfactant will interact with the water molecules and lower the surface tension of the solution. When the surface tension of a liquid is altered, liquid flows from areas of low surface tension to areas of high surface tension; a phenomenon known as the Marangoni effect.[16] Control over the droplet direction can be achieved by creating conditions under which asymmetric release of pre-loaded surfactant from the droplet occurs. Using stimuli-responsive surfactants, smart droplets have been designed which can solve complex mazes,[17] or move towards/away from a light source.[18, 19] We have investigated a number of strategies for generating spontaneous movement in droplet microvehicles based on the generation of concentration gradients of chemoattractants diffusing from a target destination within a fluidic system. Chemoattractants are chemical agents which induce positive chemotaxis in living organisms, in the same manner that chemorepellents induce negative chemotaxis. In contrast to previous studies, in which the degree of protonation of surfactant molecules underpins droplet mobility, we demonstrate spontaneous droplet movement arising from modulation of Cl^- solubility, for example, through the creation of Cl^- gradients in the aqueous phase generated from concentrated NaCl and HCl sources.

Furthermore, to our knowledge, this is the first example of the spontaneous chemotactic movement of droplets composed solely of an ionic liquid (IL) at the aqueous-air interface. The chemotactic droplets presented here consist of the IL ($[P_{6,6,6,14}][Cl]$) and a small amount of red dye (1-(methylamino)anthraquinone), which is added solely for better visualization.

Droplet movement arises due to the asymmetric release of $[P_{6,6,6,14}]^+$, a very efficient cationic surfactant, which is a

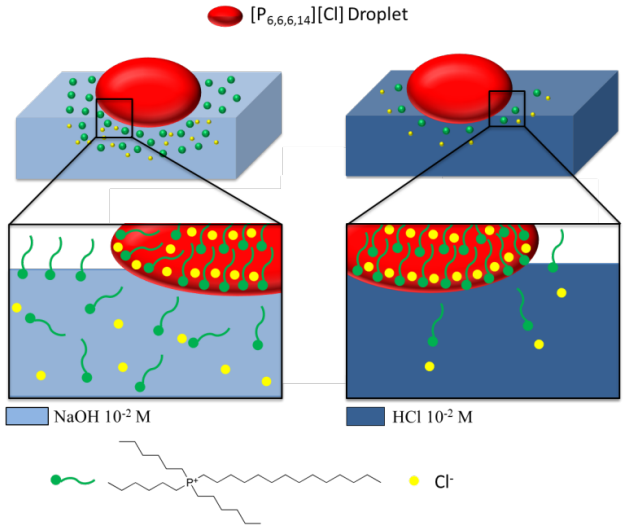

Figure 1. Diagram showing the relative solubility of $[P_{6,6,6,14}][Cl]$ droplet in solutions of 10^{-2} M NaOH (left) and solutions of 10^{-2} HCl (right).

constituent of the IL droplet. When $[P_{6,6,6,14}]^+$ diffuses from the droplet into the aqueous solution, it causes a sudden drop of the surface tension of the solution (see ESI, Table S1). The rate of $[P_{6,6,6,14}]^+$ release depends on the solubility of the closely associated Cl^- anion (ESI, Table S1), as the formation of free $[P_{6,6,6,14}]^+$ (the active surfactant at the air-water boundary) in the aqueous phase depends on the local Cl^- concentration at the IL-aqueous boundary.[20] In $[P_{6,6,6,14}][Cl]$, the Cl^- anion is strongly associated with the $[P_{6,6,6,14}]^+$ cation, rendering the IL strongly lipophilic, which enables droplets to be formed on the water-air interface. The $[P_{6,6,6,14}]^+$ cation is only sparingly soluble in water, and its partition into the aqueous phase from the IL droplet phase is strongly modulated by the local Cl^- concentration. Hence, in the presence of an aqueous phase Cl^- gradient, differential release of $[P_{6,6,6,14}]^+$ occurs and an asymmetric 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). NMR results indicate that no chemical reactions occurs between the IL and the solutions, thus movement was indeed due to biased release of surfactant (ESI, section 4).

To demonstrate this effect, three different techniques for generating the gradients underpinning 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 100 µl – 200 µl of 10^{-2} M HCl at the desired destination (See ESI video S1). For the second method the channels were again initially filled with a solution of 10^{-2} M NaOH but this time a polyacrylamide hydrogel previously soaked in 10^{-2} M HCl was placed at the desired destination (See ESI video S2). In the third approach the channels were initially filled with a solution of 10^{-5} M NaCl followed by the addition of some NaCl crystals (~ 10 mg) at the desired destination (see ESI video S3). In each case, 10 – 30 s after the addition of the chemoattractant, small droplets (~ 10 µl) of $[P_{6,6,6,14}][Cl]$ were placed at specific

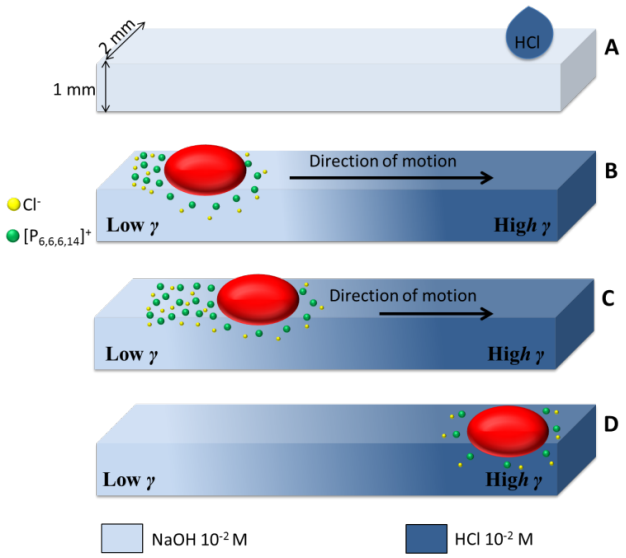

Figure 2. Schematic representation showing the movement of droplet in open fluidic channels. A – Depicts the creation of the Cl^- gradient. The channel was initially filled with NaOH 10^{-2} M solution. Then at the desired destination two or three drops of HCl 10^{-2} M solution were added (right). B – The IL was then 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 areas of highest surface tension. D – Droplet arrives at the desired destination.

locations and these spontaneously moved to the desired destination (Figure 2). As soon as a droplet is placed in the channel it begins moving along the channel towards the source of the chemoattractant traversing corners on its way. The droplet can be placed in any position within the fluidic network and in every case it spontaneously finds the chemoattractant source. In control experiments in which the chemoattractant was not added, the droplets either did not move or moved randomly due to uncontrolled release of the surfactant.

Due to the dynamics of the formation of the ion gradient along the channel(s), the time when a droplet was placed relative to the introduction of the chemoattractant, affected its speed towards the source. This was investigated by releasing a number of droplets (6 in total) at different times and at various locations along the fluidic network (Figure 3). The droplet movement was tracked using a custom-written vision system program. The gradients required for droplet propulsion were analysed using a low-cost and readily available technology,[21] see ESI. Typical speeds of the droplets estimated using this program were found to be in the range 0.5 - 4 mm/s over the first 30 seconds (See ESI Figure S6).

When droplets of the IL trihexyl(tetradecyl)phosphonium dicyanamide ($[P_{6,6,6,14}][DCA]$) was placed into the same gradients (as the $[P_{6,6,6,14}][Cl]$) no movement was observed. This behaviour can be explained through inhibition of the aqueous solubility of $[P_{6,6,6,14}]^+$ due to the DCA^- ion, which is less soluble in the aqueous phase than the Cl^- ion.[22] This interpretation is supported by the observation that no significant change of the surface tension of the aqueous solution occurs after the addition of a droplet of $[P_{6,6,6,14}][DCA]$) (See table S1).

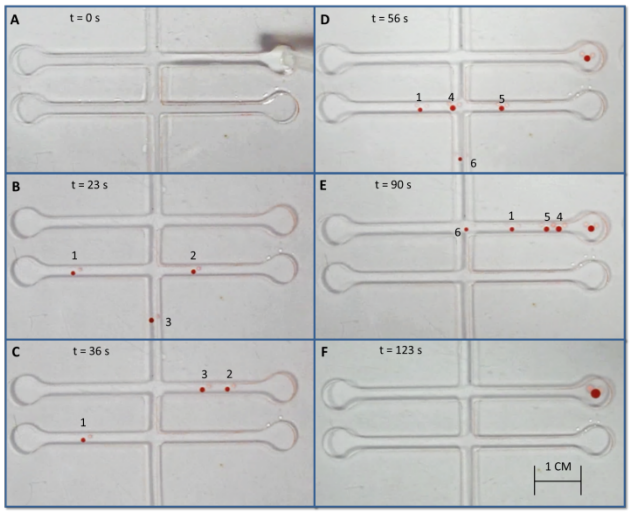

Figure 3. Sequence of video frames showing multiple droplets travelling towards source of chemoattractant. **A** – Placement of chemoattractant. (Method 1) **B** – Place of first three droplets. **C** – First two droplets moving towards source. **D** – Place of final three droplets. **E** – Movement of all droplets toward source. **F** – All droplets arrive at destination and merge.

As the partition of the sparingly soluble cationic surfactant into the aqueous phase is modulated by the solubility of the anion component of the IL, any gradient in the aqueous phase composition that affects anion solubility can be used to control droplet movement. Thus the chemotactic behaviour of the droplet is not limited to Cl^- ion gradients but is also observed with potassium bromide (KBr) and sodium sulphate (Na_2SO_4) gradients (see ESI table S1). This shows that the chemotactic movement of these droplets is affected by any factor that affects Cl^- partition from the droplet, such as the ionic strength of the solution (which also inhibits the cation solubility).

Since there is a large library of ILs available, this opens up numerous means of creating gradients for these droplets to follow. Moreover, ILs have negligible vapour pressure, low combustibility and high thermal stability.[22] These properties make them extremely useful as micro-scale "vehicles" compared to conventional organic droplets that are subject to evaporation and which can be flammable. ILs have also been shown to be good solvents for numerous chemical species and have been used in a wide range of reactions, including harsh reactions such as Grignard reactions,[23, 24] broadening the potential applications for these biomimetic chemotactic droplets.

Conclusions

In conclusion we have demonstrated a simple single component biomimetic droplet that spontaneously moves in a direction determined by an external chemical gradient. This biomimetic-type movement enables the droplets to find the pathway to the source of the chemoattractant from different initial starting positions in a microfluidic network. Since the droplets are self-propelled and spontaneously travel along the liquid-air interface by release of surfactant-type ions, they require no external energy source. It is envisioned that these droplets could be used for dynamic sensing (*e.g.* in this case they indicate the direction of increasing Cl^- concentration in the channels through their movement), energy-free molecular-cargo transport and as micro-vessels that can perform chemical reactions at pre-determined locations (*e.g.* through fusion of droplets that contain reaction precursors).

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Notes and references

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