Movement of Micrometer Sized Oil Droplets in Aqueous Solutions Follows Ion Movement

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Abstract

Cellular processes involve the movement of many forms of materials involving both active and passive processes. Described here is the phenomenon by which micrometer sized oil droplets, created with a nonionic surfactant, move spontaneously through solution being propelled by the large scale movement of ions, with hydrogen ions being able to move oil droplets across a smaller gradient. This has implications for both artificial life development as well as questions concerning the mechanisms regarding the emergence of life.

Introduction

Previous studies have demonstrated the formation of micrometer sized oil droplets and their self propelled motion in aqueous solutions particularly with the addition of hydrogen ions (Banno et al., 2013 & 2018; Lagzi et al., 2010). These studies used cationic surfactants of various types to achieve their results. These findings provide insight for generating cell type processes as well as the emergence of life.

Oil droplets have been used in a variety of approaches to study life like phenomenon. Cejkova, Hanczyz & Stepanek (2018) used decanol droplets to produce protocell structures that demonstrated appendages, movement, fusion and division. Movement of olive oil droplets in a highly basic environment was demonstrated by Armstrong & Hanczyc (2013) working off of the original work by Otto Butschli that included self organizing patterns. Motion based on pH has been reported by Ban et al. (2013) using NaOH and demonstrating movement after a certain pH threshold was achieved. Using machine learning Points et al. (2018) developed an approach to predict swarming of oil droplets in an aqueous media. Li et al. (2016) demonstrated three types of oil droplet motion that can be produced by engineering the surfaces on which they are placed. Fatty acid systems that follow chemical gradients have also been reported (Hanczyc et al., 2007). The investigations described here further explore the role of ion movement, and hydrogen ions in particular, in the movement of micrometer sized oil droplets using a nonionic surfactant.

Materials and Methods

Studies were conducted using a 3D printed modified gel electrophoresis tank (file link in appendix) with added baffles (Figure 1) and scaled to fit under a stereo-microscope (40x) (Figure 2). The gel tank consists of an elevated flat surface plate that connects to deep two side tanks through baffles that limit the effects of fluid flow. This allows either tank to be filled with a choice of solution and the center plate to then be filled with an oil-water-surfactant emulsion and the resulting behavior observed microscopically, the emulsion acting as a bridge between the two chemical tanks. The ion containing fluids are added to the side tanks until just at the level of the baffles using a transfer pipette. Then, using a pipette, the emulsion is added to the middle platform. When the emulsion bridge connects the two tanks some initial turbulence is noted in the emulsion, after which distinct movement of oil droplets can be observed. This is a very simple system that allows easy observation of oil droplet dynamics.

The stock oil droplet media consisted of 8ml mineral oil with 1ml toluene and 1ml naphtha and 40mg Sudan black B to enhance visualization. The oil-water-surfactant emulsion consisted of 40uL of the stock oil droplet medium with 10ml 1% Tween-20 a nonionic surfactant; vigorously agitated this produced a rich suspension of microscopic oil droplets ranging in size from 10µ-50µ (Figure 3).


Figure 1. Tank Prototype

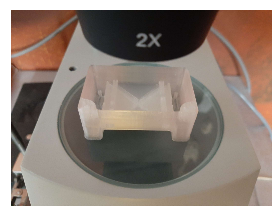

Fig 2. In Operation

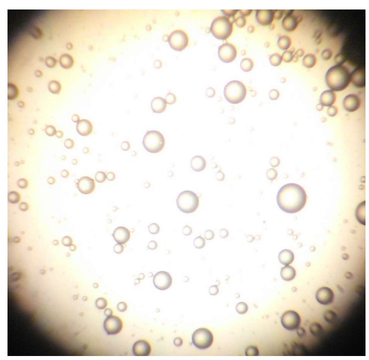

Figure 3. Oil droplets (40x)

Test solutions, placed in either tank of the modified gel system, consisted of: NaH_2PO_4 (monobasic) 1M; Na_2HPO_4 (dibasic) 1M; KH_2PO_4 (monobasic) 1M; K_2HPO_4 (dibasic) 1M; KCL 1M; NaCl 1M; NaOH 2M. Neutral red was used as a pH indicator in some tests.

Results and Discussion

When one side of the tank was filled with NaH_2PO_4 (monobasic) and the other with Na_2HPO_4 (dibasic) and the plate filled with oil emulsion there was clear and rapid motion of oil droplets to the dibasic side of the tank. Rapid movement of droplets was also reported by Ban et al. (2013) in an NaOH based system. Currently, the motion is tracked manually and is too rapid for manual measurement, automated methods are under development. This work uses fairly concentrated reagents in a manner similar to Armstrong & Hanczyc (2013). Lower reagent concentrations may result in slower droplet movement and be easier to measure, this needs to be explored further. Similarly, when one side of the tank was filled with KH_2PO_4 (monobasic) and the other with K_2HPO_4 (dibasic) there was again movement of oil droplets to the dibasic side. Na and K monobasic solutions have a pH of 4 while Na and K dibasic solutions have a pH of 8 thus the oil droplets followed the motion of hydrogen ions along the pH gradient. Switching the phosphate buffer components so that one side contained the Na cation and the other the K cation made no difference, the oil droplets always moved to the dibasic side. Adding neutral red to the system indicated that the movement of oil drops coincided with pH changes, observed macroscopically.

When both tanks were filled with distilled water only random movement was seen in the oil emulsion until HCl was added to one side and NaOH to the other, then oil droplet movement was seen headed toward the NaOH side, following the presumed movement of hydrogen ions. Similarly when one tank was filled with a HCl solution and the other side with distilled water, oil droplet movement followed the diffusion of hydrogen ions.

The effect of ion movement on oil droplets was further explored using strong diffusion gradients of NaCl and KCl. When one side of the tank was filled with either 1M NaCl or 1M KCl and the opposite tank with distilled water there was clear motion toward the distilled water side with the oil droplets following the diffusion of the salt solution.

Repeat experiments were conducted with Triton-X-100 1%, a nonionic surfactant with short side chains and a molecular weight of 647, with no directed movement of oil drops seen either with the phosphate buffer system, the HCl-NaOH system, or simple diffusion of NaCl or KCl. Tween-20 (polysorbate 20), used here, is also considered to be a nonionic surfactant, however it is a mixture of many repeating polyethylene glycol chains and molecular weight of 1226 raising the possibility that some chains may carry charges and in an electrochemically unequal environment, producing motion.

Banno et al. (2018) reported movement of oil droplets in their configuration, when exposed to UV light. Such movement, on exposure to UV light, was not seen with this configuration. Control experiments using only mineral oil without solvents or dyes did not alter the outcome of any experiments, only the visibility of the droplets.

The movement of oil droplets is not new, see Maass et al. (2016) for a review, but typically involve cationic surfactants, often Gemini surfactants. This system uses a nonionic surfactant with long side chains, as well as fairly concentrated solutions. The motion described in this system may be due to the Marangoni effects as the droplets move with the flow of hydrogen ions, the long side chains of Tween-20 potentially carrying a charge. Lagzi et al. (2010) describe motion of oil droplets along a pH gradient toward the source of hydrogen ions. The report differs here because the droplets in this system are predominantly found below the surface, decreasing surface tension effects, and the oil droplets moved with the flow hydrogen atoms, not against it. Similarly, the movement of oil droplets along simple ion gradients suggest that ion gradient motion may be more varied than previously appreciated and could be applied to a large number of systems.

Appendix

Gel Tank: https://www.thingiverse.com/thing:6646717

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