Self-propulsion of 3-Phenylpropionaldehyde droplets

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Abstract

We report a novel versatile droplet system where droplets of organic solvent, 3-phenylpropionaldehyde (3PPA), spontaneously propel themselves both on the surface of surfactant solution, that is, at the air-solution interface, and on the bottom surface of the Petri dish, that is, at the glass-solution interface. Moreover, we found that 3PPA can be polymerized with the help of basic catalysts, resulting in a compound with enhanced surface activity. This polymerized compound then alters the mode of droplets' self-propulsion. We propose that this 3PPA droplets system can be used as a primitive cell model for its ability of propulsion and chemical reaction both induced by its environment.

Introduction

Organic solvent droplets are known to sometimes exhibit spontaneous motion under non-equilibrium conditions [Lauga and Davis (2012); Ban et al. (2013); Lach et al. (2016); Tanaka et al. (2017); Michelin (2023)]. The self-propulsion of the droplets arising from local interfacial tension gradients has attracted attention as a simple model system of autonomous behavior [Pimienta and Antoine (2014); Tanaka et al. (2021)]. It has been observed that various properties inherent to living organism such as propulsion and energy conversion are realized in these systems albeit they consist of entirely non-living components [Toyota et al. (2009); van Haren et al. (2020); Watanabe et al. (2022)]. These life-like properties have potential to be used as a primitive cell model as it simplifies the characteristics of cells and mimics them with basic elements [Zwicker et al. (2017); Santiago and Simmel (2019)].

Here we report a novel versatile self-propulsion system where droplets of organic solvent, 3PPA, exhibiting motion both on the surface of surfactant solution and on the bottom surface of glass in the solution. Moreover, we observed that the introduction of amino acids in the surfactant solution triggers changes in the propulsion modes and induces oscillation of the droplet. We consider that our system can be seen as a primitive cell model because of its ability to exhibit complex life-like behavior through autonomous responses to environmental changes.

Methods

Droplets were made of pure 3-Phenylpropionaldehyde (3PPA) visualized with a dye, 5×10^{-3} wt% Oil red O. A 20 µL droplet of 3PPA, approximately 2.5 mm in diameter, was either placed on the surface of or injected into a 10 g/L sodium dodecyl sulfate (SDS) aqueous solution. Histidine (HIS) was mixed, when necessary, with the SDS solution to achieve 30 g/L HIS solution. All chemicals were analytical grade and were purchased from Tokyo Chemical Industry (Tokyo, Japan). The motion of 3PPA droplets in a quasi-one-dimensional channel (1 cm × 10 cm) was captured from side using a high-speed CMOS camera (Baumer VCXU-04C, Frauenfeld, Switzerland). The flow field around a droplet was visualized using polyethylene particles of 300 μm to 355 μm in diameter (Cospheric, California). The flow field was analyzed using ImageJ (National institutes of Health, Maryland).

Results and Discussion

Figure 1 shows flow fields around a moving droplet, on the surface of SDS solution [Fig. 1(a)], and on the glass surface in the SDS solution [Fig 1(b)]. On the surface of SDS solution, the droplet exhibited reciprocation for approximately 5 hours, whereas on the glass surface in the SDS solution the motion continued for about 30 minutes. The motion of tracer particles around these droplets is color-coded from red to blue, and the Marangoni convection near droplets is clearly visible. That is, tracers floating nearby the droplet were drawn towards the droplet and subsequently repelled from the droplet to the opposite side on the surface [Fig. 1(a)]. Similarly, when a droplet was on the glass surface in the solution, tracers were initially attracted to the droplet from above, then repelled from the droplet along the glass surface [Fig. 1(b)].

Based on the observation shown in Fig. 1, we propose following mechanism for the self-propulsion of 3PPA droplets. When a 3PPA droplet is in contact with SDS solution, SDS molecules bind to 3PPA molecules, forming complexes and solubilizing them into the solution. If these 3PPA-SDS complexes lower the interfacial tension at air-solution inter-

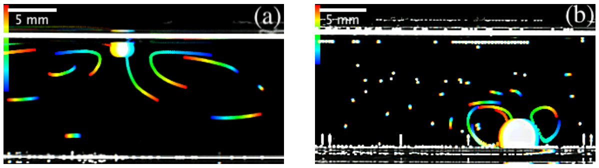

Figure 1: Time-lapse photography capturing the motion of tracer particles around a 3PPA droplet (a) on the surface and (b) on the glass surface in the solution. Positions of the tracer particles are color-coded per 0.2 s. Red is the starting point, particles move toward blue. The volume of SDS solution was 5 ml, the scale bar is 5 mm. The droplets are 10 µL and about 2mm in diameter on (a) and 40 µL and 3 mm on (b) for visualization.

face and that at oil-solution interface, the interfacial tension gradient is created depending on the amount of complexes there. On the air-solution interface, it will be high close to the droplet and low away from it. Therefore, the resulting Marangoni stress makes flow away from the droplet, which drives the droplet motion. On the glass surface, on the other hand, oil-solution interface in the direction of droplet motion is expected to have lower interfacial tension because this side of the droplet gets more SDS molecules to make complexes due to the droplet motion. Therefore, the Marangoni stress moves the interface in the opposite direction to the droplet motion, then it drives the droplet motion. In both cases, there seems to be a positive feedback between the Marangoni flow and the droplet motion.

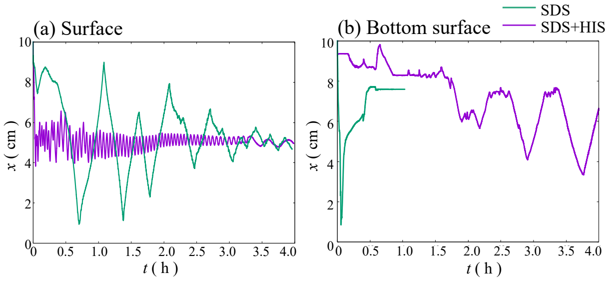

Figure 2: The position x of a 3PPA droplet in a quasi-one-dimensional channel as a function of time t. (a) On the surface of SDS solution and (b) on the glass surface in SDS solution. Green line represents motion in SDS soltuion and purple line represents motion in SDS-HIS solution.

The presence of HIS significantly altered the motion patterns as shown in Fig. 2. On the surface of solution, the 3PPA droplet exhibited short distance, short period oscillation when HIS was added [Fig. 2 (a)]. On the other hand, a longer duration of propulsion was observed on the glass surface in the SDS-HIS solution [Fig. 2 (b)]. Figure 3 shows the size reduction rate of 3PPA droplets in SDS solution with and without HIS. When HIS was added to the SDS solution, the size reduction of droplets was suppressed compared to the case without HIS.

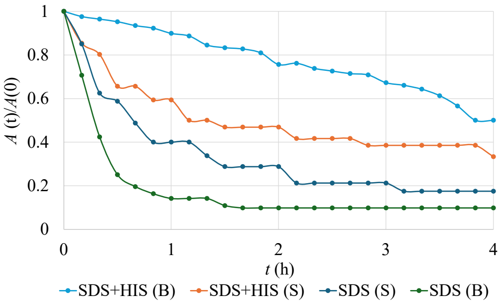

Figure 3: Size reduction of 3PPA droplets estimated using the area $A(t)$ of a droplet observed from above as a function of time t, normalized by $A(0)$.

The suppression of droplet's size reduction indicates that HIS slows down the release of 3PPA molecules into solution. We also confirmed significant increase of droplet's viscoelasticity by sticking it with a needle. This observation together with the results from nuclear magnetic resonance and mass spectroscopy suggests that the suppression of dissolution is originated from the oligomerization of 3PPA molecules occurring within the droplet, catalyzed by HIS. The suppression of dissolution can explain the extended operational lifetime of the 3PPA droplet, whereas it is still unclear how this suppression of dissolution induces the change of motion patterns such as high frequency reciprocation. In any case, the 3PPA droplets seem to capable of autonomously changing its motion pattern and energy conversion efficiency in response to the change of their environment.

Conclusions

We investigated a novel, versatile self-propelled system consisted of aldehyde (3PPA) and surfactant (SDS). Droplets of 3PPA were observed to propel themselves due to Marangoni stress. We found that 3PPA droplets are capable of moving both on the surface of SDS solution and on the glass surface in the solution. In addition, when a basic catalyst (HIS) was added to the 3PPA-SDS system, the motion of the droplets was significantly altered. On the solution surface, a characteristic smaller-amplitude, shorter-period reciprocation was induced. On the glass surface, the life time of propulsion was significantly extended. Our experimental results suggested that these changes were caused by oligomerization of 3PPA moleulcules delaying their dissolution into solution. This phenomenon, self-propulsion and its modification through chemical reaction, may be utilized to model behavior of cells adapting to environmental stimuli. It is necessary to study more this versatile droplet system in order to realize some of the characteristics that primitive cells should have.

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