Ionic Control of Droplet Motion

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We demonstrate that an aqueous droplet containing calcium ions undergoes rhythmical oscillation in an organic phase containing a surfactant of phosphate group. The same oil/water interface exhibited the self-pulsing of the electrical potential. The patterns for the rhythmical oscillation and the self-pulsing were dramatically affected by the cation species.

Chemically driven instability at liquid–liquid interfaces induced macroscopic motion of the interfaces or oscillation of interfacial tension and electrical potential.[1] When a droplet is formed in the immiscible liquid phase, the interfacial motion is observed as a spontaneous motion of the droplet. Almost all of the droplet motions are erratic and intermittent, which is known as "kicking" phenomenon.[2] However, droplets with appropriate size or under a designed boundary can show ordered motion.[3] Here, we show that an oil/water interface can detect a specific ion Ca^{2+} as the spontaneous motion of the droplet.

We carried out two kinds of experiments, i.e., experiments for spontaneous motion of the growing droplet and for measurement of the electrical potential of the interface. For the droplet motion, aqueous solution containing 1 M metal chloride was used as the droplet phase, and heptane with 5 mM di(2-ethylhexyl) phosphate (DEHPA) as continuous phase. Pendant droplet was formed at the tip of a stainless steel nozzle in a glass vessel. We kept supplying the aqueous solution to the droplet by using a syringe pump at volume flow 50 µL/min. Thus, the droplet keeps growing during the experiments. The motion of the droplets was recorded by a high-speed video camera (FASTCAM-PCI R2, Photron) from side or bottom of the vessel and analyzed by image analysis software (Movie Ruler, Photron). The electrical potential was measured with a liquid membrane interposed between two aqueous solutions with U-shaped glass tube (see Figure 2). Nitrobenzene solution (6 mL) containing 5 mM DEHPA and 0.5 mM tetraethylammonium bromide (TEAB) was placed in the base of the U cell. Two different aqueous solutions were introduced into each arm of the U cell above the oil phase. One of the aqueous phases contained divalent metal chloride and the other included NaCl. The voltage across the liquid membrane was measured with a mV meter (HB-111 and HA-151, Hokuto Denko). All reagents were commercial products of analytical grade. We confirmed the reproducibility of these experiments.

The droplet motion developed from a weak fluctuation to a vigorous oscillation as the droplet grew. When Ca^{2+} was used as the metal ion, a regular motion appeared after an induction period for an irregular motion. Most of the motion of the droplet was confined in a horizontal plane perpendicular to the nozzle. Thus, we focused on the horizontal motion, and hence the motion is expressed by the coordinate x shown in the inset of Figure 1.

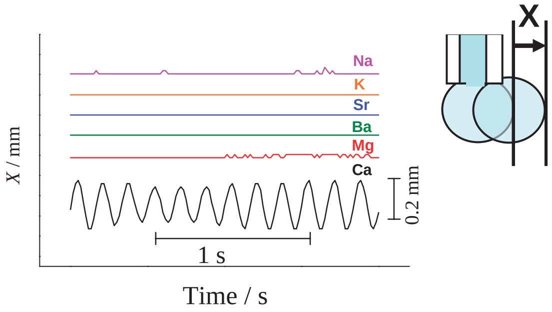

Figure 1. Evolution of droplet motion with different metal ion species. Vertical axis represents displacement of the droplet. The inset illustrates experimental setup for a water droplet containing 1 M metal chloride formed at a stainless steel nozzle in heptane containing 5 mM DEHPA at room temperature. Inner and outer diameters of the nozzle are 0.8 and 1.2 mm, respectively. Volume flow of the solvent supply is 50 µL/min.

The regular motion of the Ca^{2+}-containing droplet appeared only after the droplet grew into a large size. Figure 1 shows the displacement x with different metal chlorides after the droplet sufficiently grew. Only the Ca^{2+}-containing droplet showed a regular and sustained motion, whereas the droplet containing the other metal chlorides, Na^+, K^+, Sr^{2+}, Mg^{2+}, and Ba^{2+}, scarcely oscillated at 1 M metal chloride and 5 mM DEHPA. The regular oscillation for the Ca^{2+}-containing droplet went on until the droplet separated from the nozzle. The ion-selective motion appeared the most remarkably under this condition, although the droplets containing the other metal ions weakly oscillated under other conditions. Without metal ions, no oscillation was observed. Periodical eruption of the solute from the droplet to the surrounding media was seen during the droplet oscillation in the Ca^{2+}-containing system. The erupting phase is considered as metal ion-rich material. Stopping the solvent supply to the droplet during the regular oscillation caused the droplet motion to cease. After that, the droplet sometimes oscillated intermittently.

At a flat liquid–liquid interface, irregular oscillation of interfacial tension was observed in the Ca-containing system.[4] When the solvent supply was added to the droplet as a slight perturbation, it can induce the internal flow to form vortices in the droplet. This is already confirmed for a simpler oil/water system containing acetone as a solute.[5] The resulting self-organized flow maintained the spontaneous motions. Solution supply to the droplet is necessary for generating the regular motion.

We measured an electrical potential oscillation across a liquid membrane with U-shaped glass tube. Only the Ca^{2+}-containing system showed rhythmical oscillation of electrical potential at 1 mM metal chloride (Figure 2). The oscillation started after

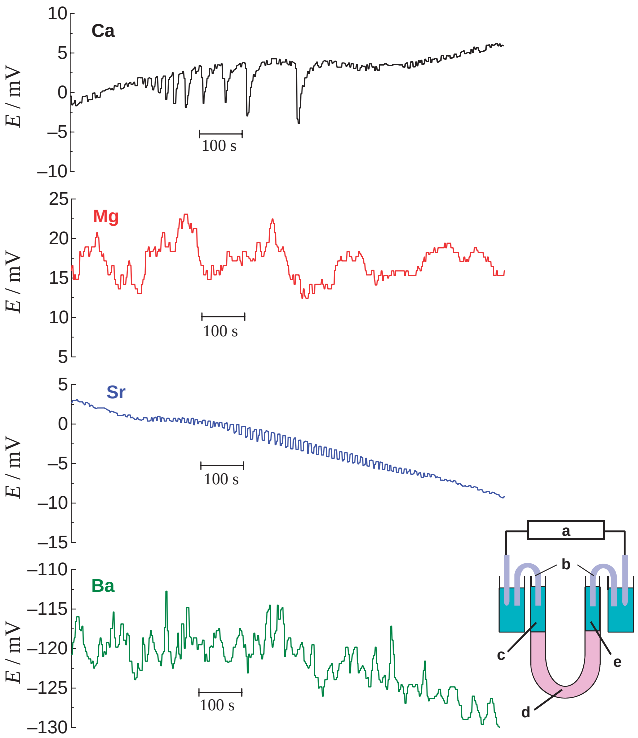

Figure 2. Electrical potential between the two phases containing divalent metal chloride and NaCl, respectively (Black line: 1 mM $CaCl_2$, red line: 1 mM $MgCl_2$, blue line: 1 mM $SrCl_2$, green line: 1 mM $BaCl_2$). The inset illustrates experimental setup for electrical potential across a liquid membrane with U-shaped glass tube (18-mm inner diameter). (a), mV meter. (b), KCl salt bridge. (c), Aqueous phase containing 1 mM NaCl. (d), Nitrobenzene containing 5 mM DEHPA and 0.5 mM tetraethylammonium bromide. (e), Aqueous phase containing different divalent metal ions.

an induction period. The other metal ions exhibited only irregular or weak fluctuations. For high concentration of metal chloride (1 M) at which the Ca^{2+}-containing droplet oscillated, relatively rhythmical oscillation was observed even in Mg^{2+}- and Sr^{2+}-containing systems (data not shown). Thus, the interface with the rhythmical potential oscillation does not necessarily correspond to the droplet with the regular motion. The electrical potential can detect the interfacial instability more sensitively than the droplet motion. This is because the droplet motion remains invisible until instability develops macroscopically to form the internal flow. Thus, the instability of electrical potential preceded that of the droplet motion. Difference of factors, such as geometry of the interface and the solution supply between the two experiments may also affect frequency and oscillatory modulation.

The occurrence of the interfacial instability relates to the reactivity between Ca^{2+} and DEHPA.[4] It is well known that DEHPA can extract metal ions from aqueous to organic phases. For 1 M metal chloride and 5 mM DEHPA, extraction ratio of Ca^{2+} is the highest value among the divalent metal ions employed in this work. Additionally, only the Ca^{2+}-containing system showed clear N-shape dependency of the interfacial pressure on DEHPA concentration. Details were described elsewhere.[4] From these results, we consider that the reactivity greatly affects the instability in electrical potential, whereas macroscopic motion of the droplet appears only when satisfying some other conditions. Emergence of the regular motion of the droplet depends on the internal flow and the eruption of solute. The mechanism why the eruption causes the regular motion will be discussed in a simpler oil/water system containing acetone.[5]

We have shown that the liquid–liquid system containing the surfactant of phosphate group can detect Ca^{2+} as a macroscopic motion. Calcium ion plays an important role in living organisms, for examples, in chemotaxis, cell–cell communication and muscle motion.[6] Superficially, the behavior in our oil/water system resemble to that of living organisms. The resemblance is not based on a common molecular mechanism. However, the present interface may provide a building block of a moving system looking like living organisms, which responds to the environmental chemical nature.

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