

Self-generated Motion of Droplets Induced by Korteweg Force

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Phase-separating droplets exhibit self-generated motion depending on the composition of the constituent solution of a biocompatible material, aqueous two phase system. For higher concentrations than the equilibrium concentration, a droplet moved unidirectionally even in a homogeneous concentration field. For lower concentrations, the droplets hardly moved. The translational motion we observed is an effect of convection caused by Korteweg force.

Chemical methods for controlling droplet motion provide the droplets with stimulus-responsive functions such as performing self-propelled motion^{1–6} or changing in the mode of motion depending on the materials in the surrounding environment.⁷ Therefore, chemical methods are considered to be the most preferable in the development of functional fluids for accomplishing particular tasks in microscopic spaces beyond the control of external forces. However, conventional chemical methods are performed by releasing the high interfacial energy inherent in the surface of a substrate^{1,4–6,7b} or droplet^{2,3,7a,7c} due to chemical reactions and by converting that gain into kinetic energy. Thus, in the former case, the droplets can move only on a specific substrate. In the latter case, the droplets inevitably consist of materials with differing chemical properties from the surrounding media to produce high interfacial energy. For use of self-propelled droplets *in vivo*, the range of application of these systems is limited. To overcome these limitations, we employed biocompatible material, aqueous two phase systems (ATPS), to make droplets move without surfactants and pretreatment of a substrate.

In our system, the interface in the initial stage does not have the driving force to propel droplets because the ATPS have quite low interfacial energy. The driving force is generated as follows. When an aqueous phase that differs from the equilibrium composition comes into contact with another aqueous phase, the composition in the vicinity of the interface changes depending on the difference between the initial and the equilibrium free energies, giving rise to a concentration gradient at the liquid–liquid interface. As a result, an interfacial energy arises at the liquid–liquid interface creating a composition-dependent force called Korteweg force.^{8–12} This force generates convective flow around the droplet, inducing motion at the center of the mass of the droplet. The fact that this method makes droplets move not by consuming energy inherent in the interface but by using interfacial energy generated by variations in the composition of the phase is a large point of difference from conventional methods. In this paper we experimentally investigate the effect of composition of the phase on droplet motion.

Experiments were performed using ATPS of poly(ethylene glycol) (PEG) + Na₂SO₄. PEG 8000 (weight-average molecular weight: $M_w = 8000$) and Na₂SO₄ (high grade) was obtained

from Wako Pure Chemical Ind., and both were used without further purification. Aqueous solution containing 13% w/w Na₂SO₄ and 10% w/w PEG 8000 was prepared and left to settle for one day in a constant temperature oven at 25 °C, separating into a lighter phase (phase L) and a heavier phase (phase H). The composition of the lighter phase L was 36.5% w/w PEG and 3.2% w/w Na₂SO₄, while the composition of the heavier phase H was 1.4% w/w PEG and 16.0% w/w Na₂SO₄ at 25 °C.¹³ When droplets of Na₂SO₄ solution with different concentrations from the phase H were injected into the phase L, droplet behavior was recorded by high-speed video camera (Keyence, VW-6000) in an air-conditioned environment at 25 ± 1 °C.

Figure 1 shows droplet motion when droplets of Na₂SO₄ solution with a higher concentration than the equilibrium concentration of phase H were formed in phase L. The droplet moved spontaneously in a straight line. The droplet retained the shape of a spherical cap and kept a constant radius while moving (Figure 1e). We found that the speed increased as the difference between the initial concentration and equilibrium concentration increased (Figure 1f). Increasing in the initial concentration leads to an increase in driving force, promoting droplet speed. The speed decreased after a few minutes had elapsed. Finally, the droplet collapsed and stopped.

We investigated flow patterns inside and outside the droplet in early stages of motion by adding activated carbon powder (Figure 2). Asymmetric flow was observed outside the droplet (Figure 2a). The tracers radiated outward from the droplet. The speed in the advancing surface increased with time just after

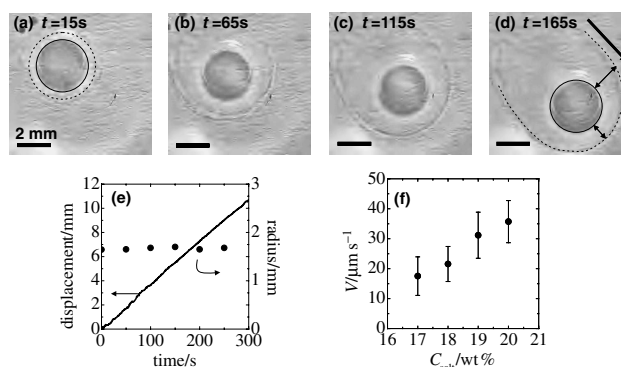


Figure 1. Self-generated motion of 10 μL droplet of 20% w/w Na₂SO₄ in phase L for the PEG + Na₂SO₄ system. In (a)–(d), the droplet moved unidirectionally. The solid and dashed lines are the periphery of the droplet and the boundary line between homogeneous and inhomogeneous refractive indices, respectively. (e) The corresponding distance from the initial position and radius of the droplet. (f) Mean speed as function of initial concentration.

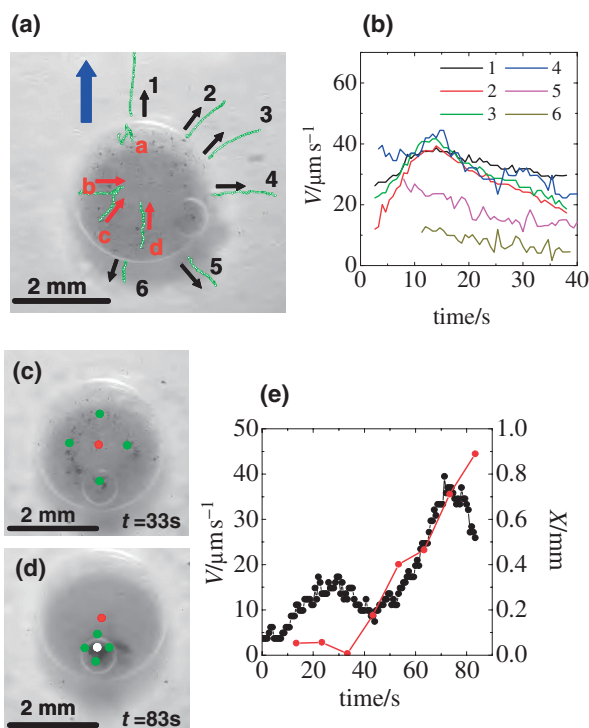


Figure 2. (a) Flow patterns inside and outside droplets of 20% w/w Na_2SO_4 in phase L. The green curves represent the trajectory of a 50-s movement of the tracer. The black and red arrows show the directions of flow outside and inside the droplet, respectively. The blue arrow represents the direction of droplet motion. The tracers outside the droplet move outward, whereas the tracers inside the droplet move inward or circulate. (b) The corresponding speed of the tracers outside the droplet. The speed of the tracers in the advancing area is higher than that of the tracers in the receding area. (c), (d) Centers of the tracer group (white circle) and droplet (red circle). The green circles are the tracers. Both positions of centers of the tracer group and droplet overlapped at $t = 33$ s, whereas distance between the centers became larger at $t = 83$ s. (e) The relation between droplet speed and distance between the centers of the tracer group and droplet. Change in the distance between the centers accelerates the droplet.

droplet formation and then decreased (Figure 2b). The speed in the advancing surface was higher than that in the receding surface. On the other hand, the tracers inside the droplet moved inward to the center of the droplet, and the other tracers near the interface circulated (Figure 2a). In the early stages, the center of the accumulated tracer group coincided with that of the droplet (Figure 2c). As time elapsed, the tracer group moved to the receding surface (Figure 2d). The distance between the centers of the tracer group and droplet affected droplet speed (Figure 2e). When the distance became larger, the droplet speed increased. On the other hand, when the distance became constant, droplet speed became almost constant.

We obtained similar experimental results by using a PEG + Dextran system. The speed of droplet motion is one order of magnitude less than that of the PEG + Na_2SO_4 system.

We found that when droplets of Na_2SO_4 solution at concentrations lower than the equilibrium concentration of

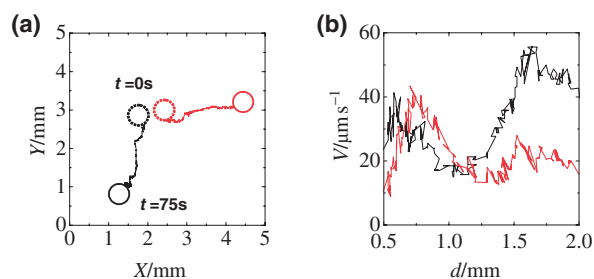


Figure 3. (a) Trajectory of two droplets of 20% w/w Na_2SO_4 in phase L. The droplets move apart from each other. (b) The relation between speed and distance between the two droplet surfaces.

phase H were formed, the droplets hardly moved in the range 10% w/w to 16% w/w. Further decreasing in the concentration below 10% w/w led to the droplets expanding to the continuous phase, and the radius of the droplets increased proportionally with the square root of time. In this case, the solutions are totally miscible. Thus, a pure diffusive process occurred.

When two droplets were formed in phase L, the droplets moved apart from each other (Figure 3). The distance between the two droplets increased with time. This repulsive behavior was observed at each concentration. Figure 3b shows the relation between droplet speed and distance between the two droplet surfaces. For a short distance, the speed of the two droplets became higher. The speed decreased with the increase in the distance. As the droplets moved apart from each other, the speed started increasing. The outward flow as shown in Figure 2a induces this repulsive behavior. For a long distance, the two droplets move independently like a single droplet system.

Vladimirova et al. conducted numerical simulations on the behavior of droplets during the phase separation in a binary system by coupling the transport of mass and momentum via the Korteweg force.⁹ The simulation showed that a single droplet moves randomly, while two droplets approach each other. The simulation results of Vladimirova also differ from our experimental results.

The directional motion in our systems can be understood intuitively as follows. Figure 1 shows the state of the area around the droplet immediately after formation. Mutual dissolution occurred around the droplet, changing the concentration of the continuous phase in the surrounding area and creating an area of differing refractive index. Isotropic distribution of concentration formed around the droplet at the initial stage (Figure 1a). If the droplet moves slightly or concentration distribution develops anisotropically, then the area over which the concentration variation extends at the advancing surface became narrower (Figure 1b). This indicates that the concentration gradient at the advancing area becomes steeper, and then the Korteweg force in this region becomes larger, further accelerating the flow of the continuous phase in this direction. In contrast, the concentration gradient at the receding area becomes gentle, and the flow in this region remains slower. The asymmetric flow can transport the droplet. The droplet motion maintains the steep concentration gradient at the advancing area. Hence, the directional motion is sustained.

In general, when phase separation proceeds in a binary mixture composed of two species *A* and *B*, an *A*-rich droplet travels toward regions with higher concentration of *A*. This attractive force can be seen as an attempt of the system to minimize its interfacial area and its free energy. Our system, however, reduces its free energy to generate Korteweg force because of coupling with hydrodynamic effects. Therefore, flow barrier screens the mutual attraction of two droplets.

For our systems, one can easily observe the self-generated motion of the droplets because the dynamics of droplets proceeds in macroscale and over a long time, whereas previous studies of Molin¹⁰ and Poesio¹¹ had some difficulties in manipulating the movement of droplets due to micrometer scale or transient phenomena. Their system consists of acetone and hexadecane. Molin showed that when a 20 μm pure hexadecane droplet was injected in acetone-rich phase, the droplet moves in the horizontal plane.¹⁰ Poesio observed dissolution dynamics of the droplets with a t^1 scaling by using 20 μm in radius droplets.¹¹ The dynamics lasts for a few second. Our systems consist of salt and polymer solution being less harmful, the dynamics can be observed in macroscale and over a long time. Thus, the systems are easier to operate. Additionally, the dynamic behavior induced by Korteweg force indicates a possibility that various kind of droplets can move spontaneously not only in ATPS used in studies other than our own, as long as the systems pass through a series of nonequilibrium states across the miscibility gap. Thus, it is possible that microcapsules, aqueous gels, vesicles, etc. impregnated with biocompatible materials will be used in biological organisms to deliver self-generated motion.

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