Microfreight Delivered by Chemical Waves

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Received: October 7, 2007; In Final Form: November 26, 2007

We report the vectorial transport of a material object to a desired location by chemical waves generated in an excitable medium (Belousov−Zhabotinsky reaction). The transportation route is determined by the excitable waves induced at a certain point on the excitable medium. This study realized direct coupling between a chemical reaction and vectorial motion; such transduction of energy is generally found in biological motility but has been difficult to achieve in artificial model systems. We discuss the future possible application of these findings to the fabrication of a chemical machine that works under the self-management of motion in response to external stimuli.

1. Introduction

Excitation waves have been observed in many phenomena in living things, such as in the propagation of excitation in nerve[1,2] and cardiac tissue,[3] in signaling processes in slime mold and other social microorganisms,[4,5] and in various physical and chemical systems under far-from-equilibrium conditions.[6,7] Chemical waves in the Belousov−Zhabotinsky (BZ) reaction have been shown to be a convenient model of spatio-temporal self-organization in excitable media.[8,9] Like biological excitation waves, chemical waves, in general, have an “informational” nature. They propagate without movement of the bulk solution, and the state of the medium, i.e., ratio of open/closed Na channels in nerves[10] and oxidized/reduced state of the catalyst in the BZ reaction,[11,12] is in fact what propagates. It has been previously shown that a chemical excitable medium can be used as an “intelligent” device that is capable of logical operations and unconventional highly parallel computing.[13−17] The notion that chemical waves are only informational in nature was recently disproved by a striking phenomenon of periodic mechanical motion of a droplet driven by the BZ reaction via microconvection.[18] In the present work, we show that chemical waves in the BZ reaction can transport objects along a desired path to a desired location. The transportation route is defined by the waves initiated from the key locations and the route and final destination can be changed by changing the timing and location of the initiation of waves. The finding that chemical waves can be used for controlled transport may enable the development of systems that use the direct coupling of information processes with transportation features. This ability might be crucial in the design of a new generation of micromachines, including lab-on-chip devices.[19−21]

Under well-stirred conditions, BZ medium shows a rhythmic change between oxidized and reduced states. When the medium is allowed to stand without stirring, chemical waves are generated spontaneously, and form target or spiral patterns, where oxidized and reduced states of the medium alternate in space and propagate at a speed of a few millimeters per minute. The waves are easily detectable and can be initiated by local perturbation, for example, with a silver electrode, electrochemically.[9,22] In a photosensitive version of the reaction, the desired pattern of propagation can be obtained simply by projecting an image onto a thin layer of the reaction medium.[17,23] These features of the BZ reaction have made it a convenient model for the study of spiral waves and other generic excitation sources and for the modeling of highly parallel computational devices.[8,13] In addition, it was recently reported that the change in interfacial tension between the oxidized and reduced states in the BZ reaction may induce convective flow.[18,24] In these studies, the authors observed the convective flow using small particles dispersed in the solution. This makes it possible to consider a propagating chemical wave not only as a “messenger” but also as a chemical engine that works under isothermal conditions. In this study, we show that small floating objects can be trapped by this flow and transported in the direction of chemical wave propagation.

2. Experiments and Results

The experimental setup is shown in Figure 1. BZ solution (220 μL) in an excitable nonoscillating state (0.15 M $NaBrO_3$, 0.3 M H_2SO_4, 0.1 M $CH_2(COOH)_2$, 0.03 M NaBr, and 5 mM $Fe(phen)_3^{2+}$) was poured into a rectangular reactor channel (45 mm × 5 mm × 1 mm). All chemicals were of analytical grade and used without further purification. An aqueous solution of ferroin, tris(1,10-phenanthroline) iron(II) sulfate, was prepared by mixing a stoichiometric amount of 1,10-phenanthroline and ferrous sulfate in pure water. After the reactor was filled, it was submerged in oleic acid. A small piece of paper (about 2 mm × 2 mm) was set afloat at the BZ reaction medium−oil interface. The chemical waves were initiated by a silver wire several minutes after the paper was placed to ensure that it did not move spontaneously. Movement of the object was observed

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10.1021/jp7097922 CCC: $40.75
Published on Web 02/02/2008

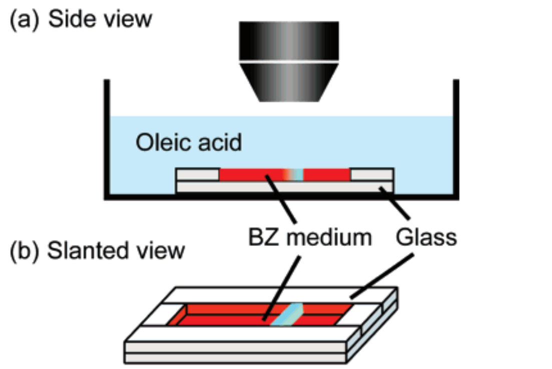

Figure 1. Schematic representation of the experimental apparatus. (a) Side view of the total system and (b) slanted view of the cell.

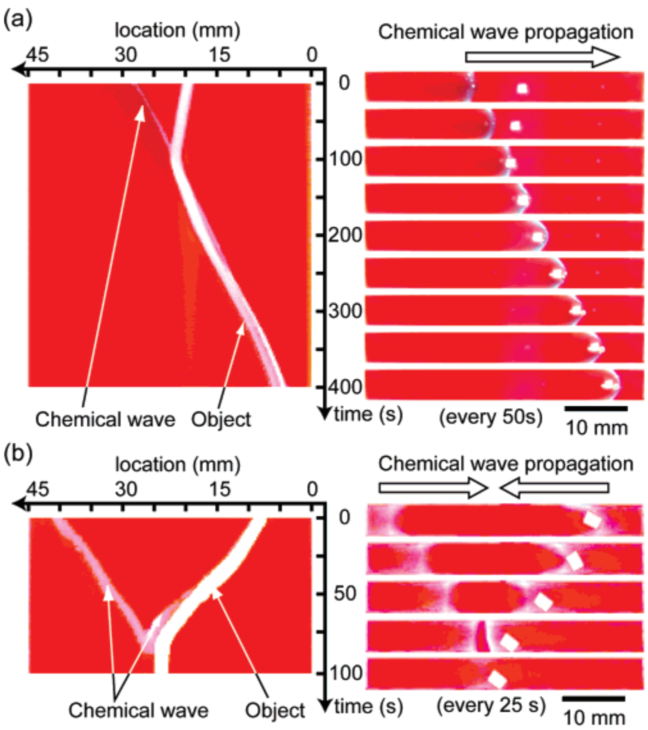

Figure 2. Consecutive positions of the BZ wave and the floating object and spatio-temporal plot representing their motion. (a) When one chemical wave is initiated, the object is transported following the chemical wave. (b) When two chemical waves are initiated, the object is transported and then stops at the position where the two chemical waves collide with each other and disappear. The interval between pictures is 50 s for a and 100 s for b, respectively. The color balance of the figures was enhanced and noise was removed with image-processing software.

and recorded from above using a digital video camera (Sony, DCR-TRV900).

Figure 2 shows two typical examples of transport of a floating object by chemical waves. In both cases, the right panel shows a series of frames extracted from the recorded movie and the left panel represents a spatio-temporal plot constructed from horizontal scans of the center of the reactor. In the series of events shown in Figure 2a, the paper was situated 20 mm from the right end of the reactor. The wave was initiated in the immediate vicinity of the left side of the reactor and propagated from left to right. The spatio-temporal plot shows propagation of the wave and movement of the object. When the wave approached within 8 mm of the piece of paper, the paper started to move toward the wave front. After a short period of initial acceleration (less than 10 s), it moved toward the approaching wave at a constant speed until it crossed the wave front, at which point it was trapped by the propagating wave and the direction of movement changed: the paper was dragged in the direction of propagation of the chemical wave, from left to right, set slightly behind the wave front. The object was transported to the end of the reactor until the carrying wave was annihilated by the boundary. There was no apparent change in the speed for the BZ wave during trapping and transport of the object. Figure 2b shows a similar series of events, but here the paper was transported from the right end to the center of the reactor. The object was dropped in the desired location by initiating a wave that propagated in the opposite direction. When the waves met and mutually annihilated each other, the dragging force disappeared and the object stood still at the delivery position.[25]

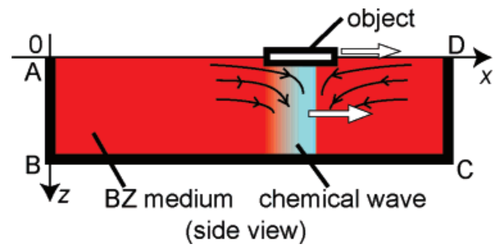

Figure 3. Schematic side-view illustration of the mechanism by which the object is dragged by a chemical wave: the difference between interfacial tension in the oxidized region and that in the reduced region induces the convective flow, which in turn traps the floating paper. The coordinates for the estimation of convective flow are also shown.

3. Discussion

The mechanism of directional transport is shown schematically in Figure 3: a local increase in interfacial tension in the oxidized region of the BZ wave results in the generation of convective flow. The paper tries to follow the flow but because it stays afloat it becomes trapped at the site where flow is directed away from the oil−water interface. When the chemical wave propagates, the trapping site moves with the wave.

Thus, transport to a desired location in a one-dimensional medium can be realized by the use of multiple waves: the carrying wave and controlling wave. This approach might also work for any continuous two-dimensional medium, since only one wave is needed to cease propagation of the carrying wave. If we vary the initiation sites and the time delay between the two waves, it might be possible to transport the object from any initial place to any desired location in a two-dimensional medium.

We can estimate the typical velocity of the transport under the assumption of a constant profile of the chemical wave. Such estimation gives the maximum value of the flow velocity. Transport is induced by convective flow due to an interfacial tension gradient, which is generated by the chemical wave.[26] The velocity profile of the BZ medium can be described using the Navier−Stokes equation with the boundary condition at the oil/water interface by imposing an interfacial tension gradient

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla p + \eta\nabla^2\mathbf{v} \tag{1}$$

$$\nabla\cdot\mathbf{v} = 0 \tag{2}$$

where $\mathbf{v}$ is the velocity profile, p is pressure, ρ is density, and η is viscosity of the fluid. The $x-z$ coordinate shown in Figure 3 is applied. The interfacial tension gradient caused by the traveling wave is introduced as a boundary condition, since the interfacial tension is greater in the oxidized state than in the reduced state. For the interface between BZ medium and oil (AD in Figure 3), the boundary condition is described as

$$\frac{\partial \gamma}{\partial x} = -\eta \frac{\partial v_x}{\partial z} \tag{3}$$

$$v_z = 0 \tag{4}$$

where γ is the interfacial tension and v_x and v_z are the components of $\mathbf{v}$ in the x and z directions, respectively. In contrast, the boundary conditions for the wall (edges AB, BC, and CD in Figure 3) should be fixed:

$$\mathbf{v} = 0 \tag{5}$$

For simplicity, the effects of the walls AB and DC are neglected.

Since the Reynolds number is estimated to be

$$Re = \frac{\rho v_x \eta}{h} \sim 0.1$$

the flow profile in this system is considered to be laminar flow, where h is the depth of the vessel. To estimate the maximum value of transport, we assume that the flow is Poiseuille-like flow and that the gradient of the interfacial tension is constant with regard to both time and space. The velocity in the x direction depending on z can be calculated as

$$v_x(z) = \frac{3G}{4h\eta}(z - h)(z - h/3) \tag{6}$$

where G is the gradient of the interfacial tension $d\gamma/dx$. Therefore, the horizontal velocity at the interface where the gradient of the interfacial tension is G can be assumed to be

$$v_x(z = 0) \approx \frac{hG}{4\eta} \tag{7}$$

In the present experimental setup, $h = 1$ mm and $\eta \sim 1 \times 10^{-3}$ kg·m^{-1}·s^{-1}. Since the change in the interfacial tension in the BZ reaction is around 1 mN·m^{-1} [26] and the typical width of the chemical wave is 1 mm, the gradient of the interfacial tension G is regarded as 1 N·m^{-2}. Using these values, we can estimate $v_x \approx 3 \times 10^{-2}$ m·s^{-1}.

The estimated value is the maximum velocity of flow induced by the interfacial tension gradient near the chemical wave front. Actually, the velocity should be decreased by the viscosity in the x direction and by the conflict with the lateral glass surface. However, since the velocity of the chemical wave is around 1×10^{-4} m·s^{-1}, which is much smaller than the estimated flow velocity, the object can catch up with the chemical wave driven by the convective flow due to the interfacial tension gradient.

On one hand, the simplified examples described above represent a new paradigm associated with chemical waves: they can be used for the transport of material objects through a desired delivery route. The combination of carrying and controlling waves with the proper timing of initiation allows us, in principle, to deliver freight over a chosen path, with the ability to switch the path if desired. On the other hand, chemical waves used for transport might share an important characteristic with living things: in living organisms, vectorial work is generated through the dissipation of chemical energy under isothermal conditions. In general, a chemical reaction can be described by a mass-action law, i.e., the kinetics can be represented as a function of scalar variables. According to the Curie−Prigogine principle, coupling between scalar and vectorial variables is prohibited under isotropic conditions within the framework of linear nonequilibrium theory.[27,28] The intrinsic mechanism of direct energy transduction from scalar chemical energy into vectorial mechanical work has been a longstanding problem in natural science and technology. In the present study, the chemical reaction can sustain the directed motion of material objects due to the fact of inherent symmetry-breaking in nonlinear reaction-diffusion systems. The direction and speed of motion are defined by the propagating wave. It has been shown that the convective flow induced by the difference in interfacial tension associated with a propagating BZ wave does not depend on gravitational forces.[18] This means that the transport of a material object by a chemical wave is a universal phenomenon which requires the following general conditions: (1) the existence of a chemical wave, (2) the maintenance of an interface along which the wave propagates, and (3) the existence of a difference in the local interfacial tension for different regions of the propagating wave which will maintain convective flow.

4. Conclusion

The vectorial transport of a material object by chemical waves in the BZ reaction was achieved experimentally, and its mechanism was discussed. Although the described mechanism of chemomechanical energy transduction is based on the particular chemistry of BZ waves, the requirements for this transduction are very general and can easily be satisfied in several nonlinear systems. The possibility of delivering microfreight over a desired route by easily programmable carrying and controlling waves might be useful in the design of the next generation of lab-on-chip devices.

Acknowledgment. The authors would like to thank Professor S. Nakata (Nara University of Education, Japan) for his helpful advice. This work was supported in part by a Grant-in-Aid for Young Scientists (B) to H.K. (No. 18740231) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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