Characteristic Self-Motion of a Camphor Boat Sensitive to Ester Vapor

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Received September 6, 2004. In Final Form: November 4, 2004

As a simple example of an autonomous motor, the self-motion of a camphor boat on water with changes in chemical stimuli was investigated. The nature of the self-motion of a camphor boat changed characteristically with the addition of ester vapor (methyl *n*-butyrate) to a circular water chamber. Thus, continuous motion changed to oscillatory motion, and its period increased depending on the location between an ester droplet and the chamber, *L*. The surface tension in the water chamber was measured to clarify how the velocity of the self-motion changed with *L*. The nature of the self-motion is discussed in relation to the surface tension as the driving force. We believe that the present results may be useful for realizing artificial chemotaxis systems under nonlinear and isothermal conditions.

1. Introduction

The self-sustaining motion of liquid droplets,[1−8] solid grains,[9,10] and gels[11,12] has been investigated with simple experiments in attempts to understand nonequilibrium systems and to develop novel chemomechanical transducers under isothermal conditions. The driving force of the motion of a droplet or solid grain at an immiscible interface is generated by Marangoni flow, which is induced by nonuniformity of the concentration distribution around the droplet or grain.[13,14] The direction of this motion and its velocity depend on the concentration gradient of the surface active molecular layer on the solid surface in contact with the droplet or at the air/water interface around the solid or droplet.

We have investigated systems with camphor which show various natures of self-motion, e.g., unidirectional motion depending on the shape of the camphor fragment,[10] mode-switching depending on the shape of the water chamber,[15] and synchronized sailing between two camphor boats.[16] It has also been shown that camphor derivatives exhibit characteristic self-motion.[17,18] The essential features of this self-motion can be reproduced by a computer simulation.[10,15−17]

In the present study, we found that the nature of the self-motion of a camphor boat on water changed with the addition of ester vapor as a chemical stimulus. Continuous motion changed to oscillatory motion and finally to no motion depending on the location of the ester vapor dropped on the system. Such characteristic motions are discussed in relation to experimental results regarding the surface tension in the water chamber.

2. Experimental Section

(+)-Camphor and other chemicals were obtained from Wako Pure Chemical Industries (Kyoto, Japan). Water was first distilled and then purified with a Millipore Milli-Q filtering system. A camphor boat was prepared as follows. (1) Camphor grains were packed into a pellet die set (3 mm diameter, 1 mm thick). (2) The resulting camphor disk was connected to a polyester plastic boat (0.1 mm thick, 2 mg mass). The camphor boat was floated on the water surface in a circular chamber, which was made of Teflon (5 mm wide; 3 mm thick; 25 mm inner radius).[16] All of the experiments were performed at room temperature. Movement of the camphor disk was monitored with a digital video camera (Sony DCR-VX700, $^1/_{30}$ s minimum time resolution) and then analyzed by an image-processing system (Himawari, Library Inc., Japan). To measure the surface tension of water, a platinum wire (diameter: 0.5 mm) was used as a Wilhelmy plate.[19]

3. Results and Discussion

Figure 1 shows snapshots of the self-motion of a camphor boat at different L values ((a) 10, (b) 5, (c) 3, and (d) 2 mm), where L is the minimum distance between a droplet of methyl n-butyrate (40 μL) and the water chamber. Figure 2 shows the time development of the velocity of a camphor boat at different L. Figure 3 shows the relationship between the velocity and θ in the circular chamber. When L was over 10 mm, the velocity of the motion was almost constant, i.e., self-motion was not greatly affected by the addition of methyl n-butyrate (see Figures 1a, 2a, and 3a). At L = 4−10 mm, oscillatory motion was observed, i.e., the camphor boat decelerated when it approached to the droplet of methyl n-butyrate ($\theta = \pi$) but accelerated when it passed through $\theta = \pi$ (see Figures 1b, 2b, and 3b).

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10.1021/la047776o CCC: $30.25
Published on Web 12/24/2004

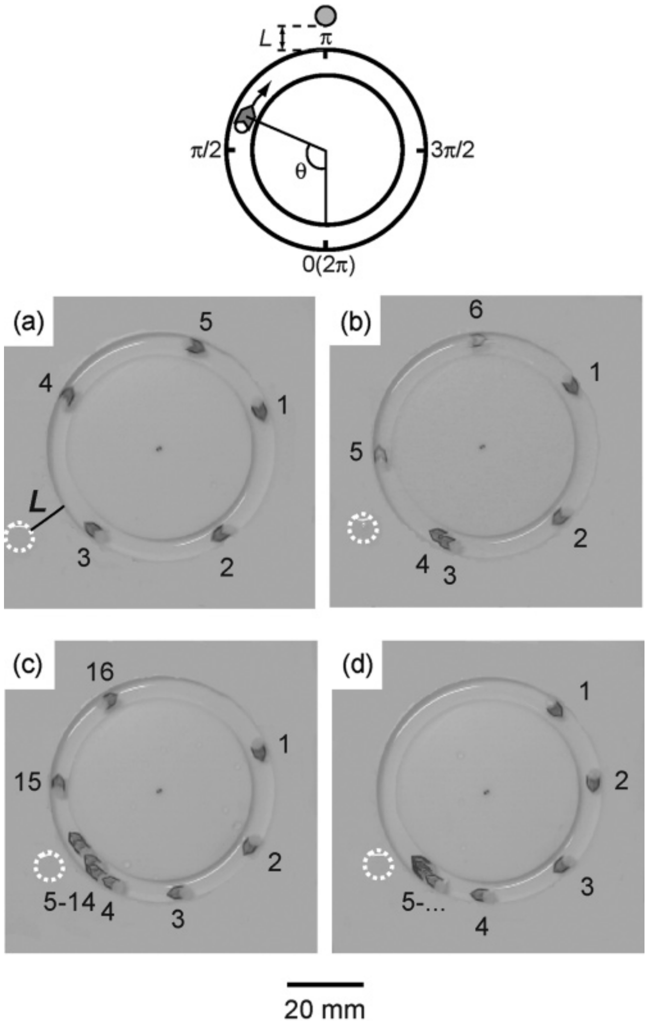

Figure 1. Snapshots of the self-motion of a camphor boat in a water chamber for L = (a) 10, (b) 5, (c) 3, and (d) 2 mm with the addition of a methyl n-butyrate droplet, which is surrounded by a dotted white circle (top view, time interval $^1/_3$ s). Above the snapshots, polar coordinates are schematically defined to analyze the motion. The angle, θ, is defined as π when the boat passes through the droplet, which is shown as a gray circle.

The amplitude of the oscillation increased with a decrease in L. Intermittent motion, i.e., alternation between rest and motion prior to $\theta = \pi$, was observed at $L = 3-4$ mm (see Figures 1c, 2c, and 3c). When L was lower than 3 mm, the boat completely stopped prior to π (see Figures 1d, 2d, and 3d).

Figure 4 shows the surface tension of water chamber, Γ_L, depending on θ at different L. The surface tension approached to a minimum value at $\theta = \pi$ and a maximum value at $\theta = 0$ (or 2π). The baseline of Γ_L versus θ curve increased with L, but the difference between the minimum and maximum values decreased with L. For $L = 2$, the surface tension at $\pi/4$ to $7\pi/4$ was lower than that behind the camphor boat (62 mN m^{-1}). For $L = 3$, the surface tension at near π was close to that behind the camphor boat.

On the basis of the experimental results, we can discuss the characteristic nature of the self-motion of a camphor boat depending on the location of an ester droplet, L, as suggested by Figure 5. First, the driving force of the self-motion of a camphor boat on a water chamber without ester is the difference in surface tension between the bow and stern of the camphor boat, $\Gamma_{c-max} - \Gamma_{c-min}$ (=66.5 − 62.0 = 4.5 mN m^{-1}).[16] The uniform motion in Figure 5a

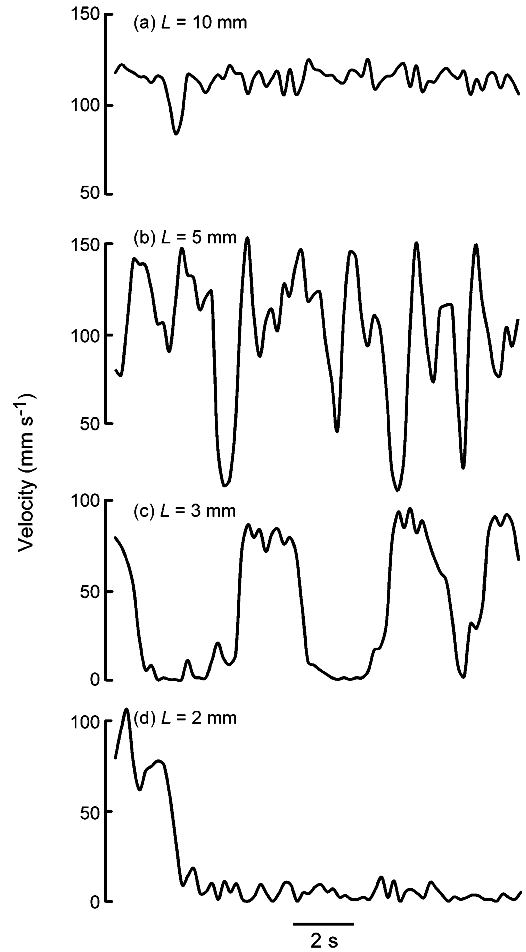

Figure 2. Time variation of the velocity of self-motion of a camphor boat in the water chamber at different L ((a) 10, (b) 5, (c) 3, and (d) 2 mm) with the addition of methyl n-butyrate. Here, θ is the polar coordinate of the location of the camphor boat on the water chamber, and $\theta = 0$ is the location of the methyl n-butyrate droplet. The data analyzed in (a−d) correspond to those in (a−d) in Figure 1, respectively.

suggests that the driving force is constant.[10] Methyl n-butyrate decreased the surface tension at $L = 10$ mm, $\Gamma_{10}(\theta)$; however $\Gamma_{10}(\theta)$ was either nearly equal to or larger than Γ_{c-max} (see Figure 4). Therefore, the difference in the surface tension, $\Gamma_{c-max} - \Gamma_{c-min}$, may continue to be the driving force for nearly uniform motion even with the addition of methyl n-butyrate.

The oscillatory motion in Figure 5b suggests that the driving force changes in an oscillatory manner. For L = 5 mm, $\Gamma_{c-min} < \Gamma_5(\theta) \leq \Gamma_{c-max}$; i.e., the driving force corresponds to $\Gamma_5(\theta) - \Gamma_{c-min}$. Therefore, the velocity alternated between deceleration when θ was close to π and acceleration when θ passed through π. The finding that acceleration around $\theta = \pi$ is greater than deceleration may be due to the anisotropy of the camphor boat.

The intermittent motion in Figure 5c suggests that the driving force is zero or slightly negative at $\theta \sim \pi$ but positive elsewhere. When the camphor boat is close to $\theta = \pi$ at L = 3 mm, $\Gamma_3(\pi - \delta\pi) = \Gamma_{c-min}$; i.e., the camphor boat stops and settles at $\theta \sim \pi - \delta\pi$. When $\Gamma_3(\pi - \delta\pi) - \Gamma_{c-min}$ becomes tentatively positive due to fluctuation of the diffusion of ester vapor within a narrow region ($\theta \sim \pi$), the camphor boat can pass through $\theta = \pi$, and the driving force for the camphor boat then becomes $\Gamma_3(\pi + \delta\pi) - \Gamma_{c-min} > 0$. Thus, intermittent motion may repeat due to the alternation of $\Gamma_3 > \Gamma_{c-min}$ and $\Gamma_3 = \Gamma_{c-min}$ around $\theta = \pi$, as seen in Figure 4. For L = 2 mm, the region of θ under the condition of

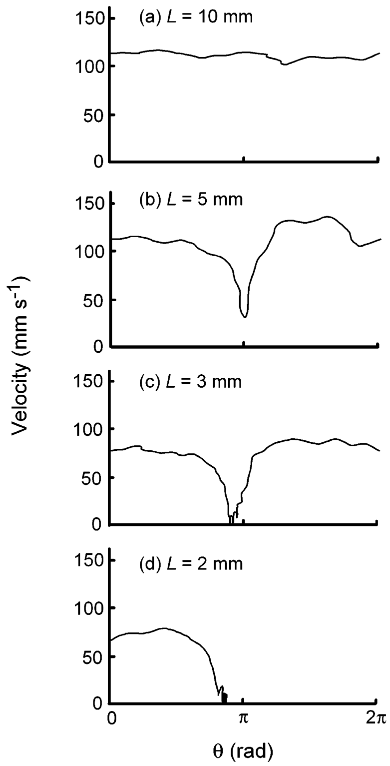

Figure 3. Velocity versus θ curve at different L ((a) 10, (b) 5, (c) 3, and (d) 2 mm) with the addition of methyl n-butyrate. The data analyzed in (a–d) correspond to those in (a–d) in Figure 1, respectively.

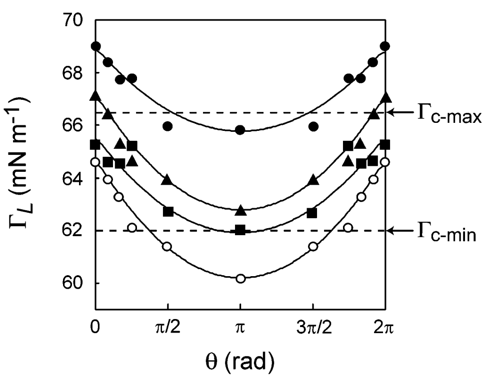

Figure 4. Surface tension in the water chamber, $\Gamma_L(\theta)$, exposed with ester vapor at different L ((filled circle) 10, (filled triangle) 5, (filled square) 3, and (empty circle) 2 mm). Dotted lines at 62 and 66.5 mN m^{-1} show the surface tension at the stern (Γ_{c-min}) and bow (Γ_{c-max}) of the camphor boat when the camphor boat was fixed to the surface of the water chamber.

$\Gamma_2(\theta) < \Gamma_{c-min}$ becomes wide; i.e., intermittent motion changes to no motion with a further decrease in L. Thus, the self-motion changes characteristically since the difference in surface tension around the camphor boat, which corresponds to the driving force, changes with the diffusion of ester vapor.

4. Conclusion

The characteristic motion of a camphor boat with the addition of ester vapor was experimentally demonstrated

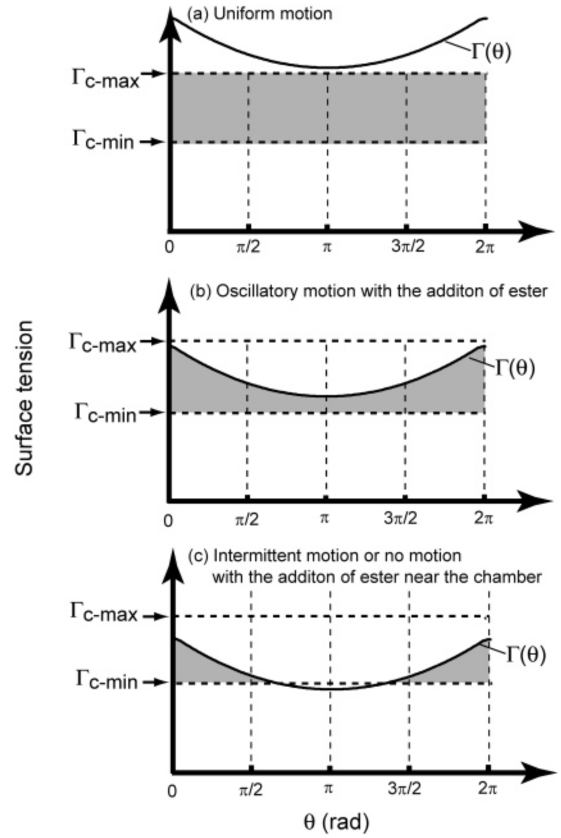

Figure 5. Suggested model for describing the mechanism of characteristic self-motion ((a) uniform motion, (b) oscillatory motion, and (c) intermittent or no motion) depending on the location of ester vapor based on the spatial surface tension in the water chamber. $\Gamma_L(\theta)$ is the surface tension in the water chamber with the addition of ester vapor at L mm and θ rad. The gray area corresponds to the magnitude of the driving force depending on θ.

in a water chamber. Such motion was discussed in relation to the surface tension as the driving force and the spatial diffusion of the ester vapor in the water chamber. The present results suggest that the self-motion changes characteristically depending on the structure of the chemical stimuli which can spatiotemporally change the surface tension in the water chamber, as in an artificial chemotaxis system. We believe that the present experimental system not only is simple but also may be useful for experimentally and theoretically creating various types of mode emergence by introducing nonlinear and nonequilibrium conditions to the anisotropic systems.[20]

Acknowledgment. We thank Mr. Shin-ichi Hiromatsu (Nara University of Education) and Mr. Hiroyuki Kitahata (Kyoto University, Japan) for their helpful discussions regarding the mechanism of self-motion. This study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 16550124) to S.N.

LA047776O

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