

pH-Sensitive Self-Motion of a Solid Scraping on an Aqueous Phase

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The self-motion of a solid scraping at an air/water interface was investigated. The self-motion of a camphoric acid scraping changed characteristically depending on the pH of the aqueous phase. With an acidic aqueous phase, the camphoric acid scraping maintains a fairly constant velocity. At neutral pH, intermittent motion was observed. These characteristic motions are discussed in relation to the surface free energy which results when the camphoric acid layer diffuses from the scraping. The nature of the diffusion of the camphoric acid layer at the water surface could be observed by adding CaSO₄ powder. These results imply the realization of chemomechanical energy transduction under isothermal conditions.

Introduction

There are several types of motor organs, or organelles, in living organisms. All of them work through the dissipation of chemical energy under almost isothermal conditions. On the other hand, several artificial systems which exhibit self-motion have been studied both experimentally and theoretically under almost isothermal conditions.^{1–12} Such motion is observed under nonequilibrium conditions, e.g., chemical or thermal inhomogeneity. The development of such a chemical engine, which works under isothermal conditions, is an important step in the creation of a novel chemical motor or artificial actuators which are capable of self-movement.^{1,10–12}

More than a century ago, the self-motion of small camphor scrapings floating on water was explained by Van der Mensbrugghe as being due to the diminished surface tension of water.¹³ Subsequently, Rayleigh studied the retarding effect of contaminating oily substances on the self-motion of a camphor scraping.¹³ Since then, there have been several experimental trials to explain these observations. We previously reported that (1) the frequency of self-rotation depends on the temperature, surface tension, and chemical structure of the camphor derivatives, (2) the direction of rotation, either clockwise or counterclockwise, is determined by asymmetry in the shape of the solid camphor scraping, and (3) the essential features of the motion of a camphor scraping could be reproduced by a computer simulation.¹² We believe that experiments on such motion imply the realization of chemomechanical energy transduction under isothermal conditions.^{2–12} In a related experiment, Yoshikawa and Magome recently examined spontaneous vectorial movement in an oil–water system by introducing asymmetry to the shape of the rotor.¹¹ In this study, the self-motion of a camphoric acid scraping changed characteristically depending on the pH of the underlying aqueous phase.

Experimental Section

Camphoric acid was obtained from Wako Chemicals (Kyoto, Japan). When necessary, fragments of camphor were produced

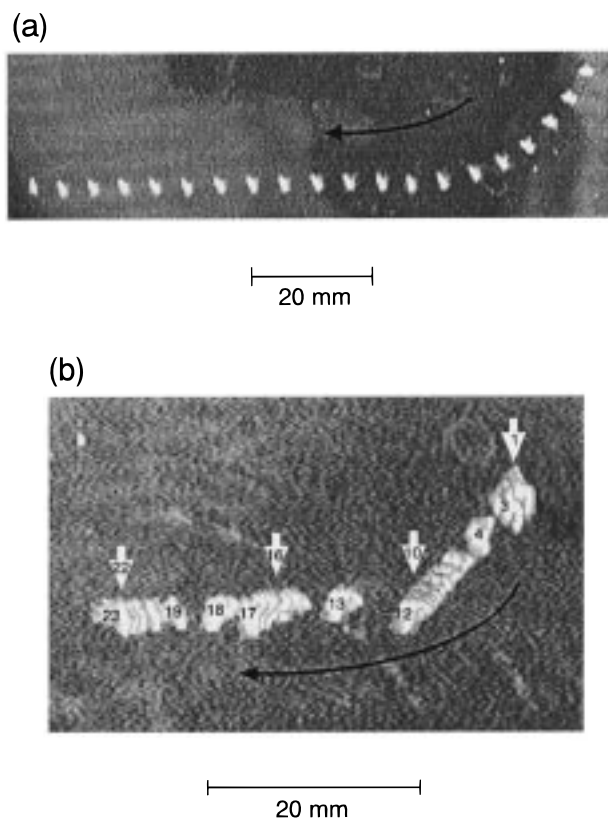


Figure 1. Time trace of the motion of a camphoric acid scraping with a time interval of 0.1 s (top view) on an aqueous phase ((a) pH 2.0, (b) pH 7.0). The scraping moved from right to left as marked by a closed arrow in each figure. The scraping rested at the time indicated by the downward open arrows in (b). The traces with a time interval of 0.1 s are numbered from 1 to 23 in (b).

in asymmetric shapes. Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water: 6.3). A phosphate buffer solution (ionic strength: 0.2) was used for the aqueous phase. A camphoric acid scraping (diameter: ca. 1.0 mm) was dropped onto an aqueous phase (100 mL) in a Petri dish (inner diameter: 150 mm). The movement of camphor was monitored with a digital video

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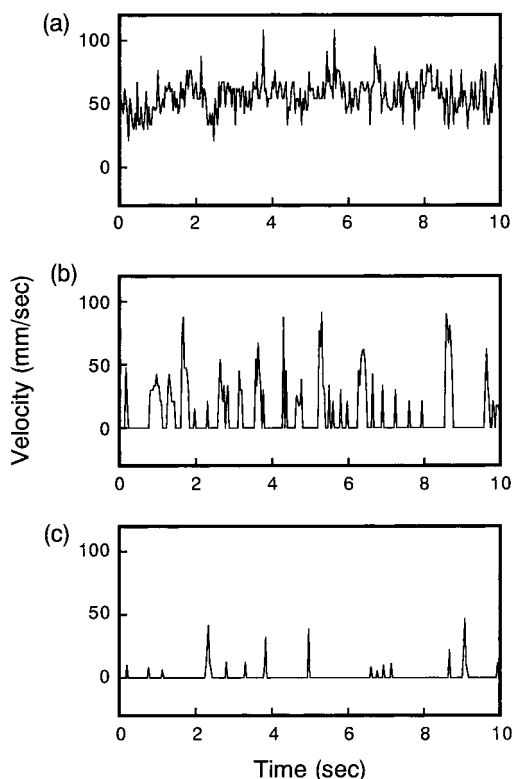


Figure 2. Velocity of a camphoric acid fragment (diameter: ca. 1 mm) on phosphate buffer solutions of various pH (ionic strength: 0.2). The pH of the bulk-aqueous phase was buffered at (a) 2.0, (b) 7.0, and (c) 12.0. The velocity was obtained from the motion of camphoric acid in the *x*- and *y*-axes.

camera (Sony DCR-VX700) and recorded on videotape at 293 ± 1 K. The two-dimensional position of the camphor was measured using a digitizer. The velocity was deduced from the simple difference of the positions in the successive video frames divided by the minimum time resolution (1/30 s).

Results and Discussion

Figure 1 shows the time trace of the motion of a camphoric acid scraping with a time interval of 0.1 s (top view) on an aqueous phase ((a) pH 2.0, (b) pH 7.0). In general, a scraping of camphor or its derivatives (camphoric acid, borneol, or camphanic acid) exhibits not only translational but also rotational motion, and the frequency, radius of orbital motion, and other characteristics of camphor motion depend on the shape and size of the camphor scraping.¹² With an acidic aqueous phase, the camphoric acid scraping maintains a fairly constant velocity, as seen in Figure 1a. At neutral pH, intermittent motion was observed, as seen in Figure 1b.

Figure 2 shows the time-course of velocity for a camphoric acid scraping depending on the pH of the aqueous phase. Here, the translational velocity of the scraping was taken and the angular velocity was ignored to simplify the analysis. Indeed, the angular velocity was relatively low owing to the morphology of the scraping selected in this experiment. At pH 2.0, the velocity was almost constant. At pH 12.0, motion was hardly observed. If the scraping exhibited rotation, the angular velocities at pH 2 and 7 were almost constant and intermittent, respectively. That is, the translational motion may correlate with the rotational motion since the interfacial morphology of the scraping contact to the aqueous phase may be varied even

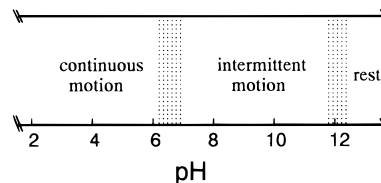


Figure 3. Phase diagram of the mode of camphoric acid motion depending on the pH of the aqueous phase. “Continuous motion” and “intermittent motion” correspond to (a) and (b) in Figure 1, respectively.

with the same scraping when it is tilted at the air–water interface. Figure 3 shows a phase diagram of the mode of camphoric acid motion depending on the pH of the aqueous phase. In this figure, “continuous motion” and “intermittent motion” correspond to (a) and (b) in Figure 1, respectively. “Rest” implies that the solid scraping hardly exhibits self-motion.

These characteristic motions depending on pH may be due to the degree of dissociation of the carboxyl group in the camphoric acid layer at the air/water interface. We can discuss the mechanism of camphoric acid motion based on that of camphor motion^{12,13} and the experimental results in the present paper.

At a higher pH, the dissociation of carboxylic acid in the camphoric acid layer may reduce the driving force of this motion because the camphoric acid layer readily dissolves into the bulk water phase, and it is then difficult to maintain the difference in the surface free energy around the camphoric acid scraping. At a lower pH, the camphoric acid layer does not readily dissolve into the bulk water phase. This insoluble camphoric acid layer produces a difference in the surface free energy to induce self-motion. The nearly constant velocity suggests that the driving force of this motion is constant; i.e., the spatial inhomogeneity of the camphor layer is maintained by the scraping. At a neutral pH, intermittent motion is observed due to a periodic change in the surface tension which may be caused by the repeated formation and loss of a camphoric acid layer at the air–water interface. The nature of the diffusion of the camphoric acid layer at the water surface could be observed by adding CaSO_4 powder, as shown in Figure 4.¹² The diameter of diffusion around the scraping at pH 2.0 remained fairly constant at 5 mm. On the other hand, the diameter at pH 7.0 was ca. 0 and 3 mm when the scraping rested and moved, respectively.

The mechanism of the periodic change in the surface concentration of the camphoric acid layer may correspond to the spontaneous oscillatory phenomena seen at an oil–water interface.^{4,11,14,15} First, the concentration of the thin layer with camphoric acid increases at the air–water interface. When the concentration of the thin layer at the interface reaches an upper critical value, the camphoric acid molecules are abruptly transferred to the water bulk phase with the formation of micelles or micro emulsions. After the concentration of the thin layer decreases below a lower critical value, the thin layer again begins to accumulate and the cyclic repeats for several iterations. According to the two-dimensional van der Waals equation for the surfactant molecules at an interface, an “N”-shape relationship is expected for a plot of the surfactant pressure against the concentration of the surfactant molecules.^{14,15} This “N”-shape relationship is associated with various oscillatory phenomena in far-from-equilibrium conditions.

In addition to the effect of the gradient in the surface tension, a solutocapillary effect (or soluto-Marangoni effect), which involves surface convection from low to high surface tension,

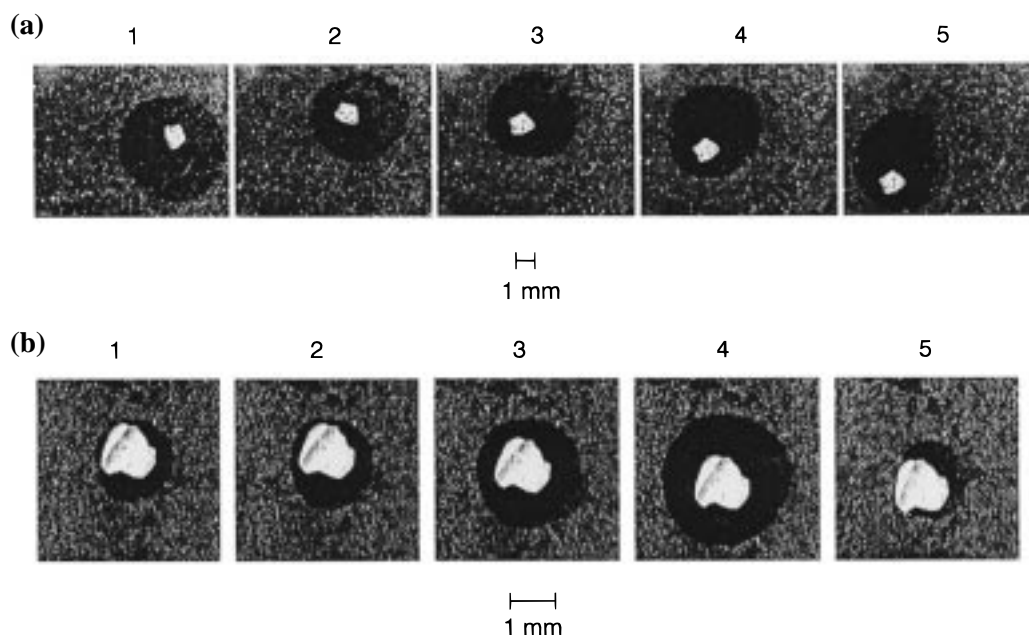


Figure 4. Snapshots of the diffusion of the camphoric acid layer at the aqueous phase with a time interval of 0.2 s (top view) at (a) pH 2.0 and (b) pH 7.0. CaSO_4 powder was spread over the aqueous surface before the placement of camphoric acid. The clear and white parts correspond to aqueous surfaces with and without the camphoric acid layer. To observe only the diffusion of the camphoric acid layer from the fragment, the camphoric acid fragment was fixed on the aqueous phase in this experiment.

should also be considered as an important factor in camphor motion.^{16–18} The effect of surface convection, due to the gradient of the surface tension, is induced by the absence of slip between the peripheral edge of the particle lying in the interface and the interfacial liquid, and bulk motion will be induced by the absence of slip between the surface of the particle at the air–water interface and the liquid below it. Actually, we noticed the convective motion of fluid induced by the capillary effect in our experiment.

According to the Curie–Prigogine theorem,^{19–21} vector processes cannot couple with scalar variables, such as an ideal chemical reaction, in a “linear” system under isotropic conditions. This implies that chemomechanical coupling becomes possible with a violation of either the linear or isotropic conditions. Thus, it may be natural to expect that effective chemomechanical coupling can be realized in the absence of both linear and isotropic conditions.¹¹ In this study, we have demonstrated that the spatiotemporal characteristics of motion change depending on the outer environment due to a gradient in the chemical energy and the discontinuous transfer of substances.

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