

Self-motion of a camphoric acid boat as a function of pH of aqueous solutions

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Abstract

The mechanism of the self-motion of a camphoric acid boat depending on pH of aqueous solutions was investigated. The self-motion changed depending on pH of the aqueous phase (no motion (pH > 10), intermittent motion (pH 6–10), and motion with a constant velocity (pH < 6)). The period of intermittence increased with pH. The surface tension in the camphoric acid aqueous solutions with different pH were measured by means of the maximum bubble pressure method and the Wilhelmy method. The camphoric acid concentration-dependencies of the surface tension and the time-variation of the surface tension at different pH were discussed in relation to the manner of self-motion and the nature of the surface active camphoric acid layer. The driving force of the self-motion was estimated by analyzing the self-motion. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Studies of artificial systems which mimic living ones may help to understand biological phenomena and to create biological functions. All motor organs or organelles in living organisms work through the dissipation of chemical energy under almost isothermal conditions and without harmful products. Internal combustion engines, on the other hand, function under strongly non-isothermal conditions. Therefore, understanding of

chemo-mechanical transduction in biological motors is important for designing novel artificial motors, which adapt to the environment and maintain the material cycle on the earth. Several artificial systems, which exhibit self-motion under conditions of chemical non-equilibrium have been studied experimentally [1–10] and theoretically [11–14] under almost isothermal conditions.

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. Subsequently, Rayleigh studied the retarding effect of contaminating oily substances on the self-motion of a camphor scraping [15]. Since then, several

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experiments have been conducted to explain these observations [16,17]. We previously reported that the manner of self-motion of a camphor scraping is changed depending on the internal conditions (e.g. scraping morphology and chemical structure) and on the external conditions (e.g. temperature, surface tension, and the shape of cell) and that the essential features of the self-motion could be reproduced by a computer simulation [19–22]. Recently, we reported that a camphoric acid scraping experimentally and theoretically changes the mode of self-motion depending on the pH of the aqueous phase (the motion with a constant velocity at an acidic pH, the intermittent motion at a neutral pH, and no motion at an alkaline pH) [21,22]. However, it has not yet been clarified why the self-motion changes its mode depending on pH.

In the present experiments, the camphoric acid concentration-dependencies of surface tension and the time variation of the surface tension were characteristically changed depending on pH of the aqueous phase. The nature of the diffusion of the camphoric acid layer at the aqueous surface was observed by adding CaSO_4 powder. The driving force of the self-motion was estimated by the analysis of the self-motion of a camphor boat. These results are discussed in relation to the mechanism of the characteristic self-motions depending on pH.

2. Experimental section

Camphoric acid and other chemicals were obtained from Wako Chemicals (Kyoto, Japan). Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water, 6.3; the resistance of water, $> 20 \text{ M}\Omega$). A phosphate buffer solution (ionic strength, 0.2) was used as the aqueous phase.

A camphoric acid scraping (diameter, ca. 1.0 mm), which was connected to a polyester plastic boat (thickness, 0.1 mm), was dropped onto an aqueous phase (100 ml) in a petri dish (inner diameter, 200 mm) to obtain only the translational motion without rotation. To obtain a good reproducibility of the phenomenon, the same

camphoric acid boat was prepared, i.e. the size and shape of the scraping, and attached situation of the scraping to the boat are almost the same as in each experiment. The contact line at the scraping/aqueous interface was ca. 1 mm.

The movement of the camphoric acid scraping was monitored with a digital video camera (SONY DCR-VX700) and recorded on videotape at $293 \pm 1 \text{ K}$. The two-dimensional position of the camphoric acid and the center of gravity for rotation were measured using a digitizer. The minimum time resolution was $1/30 \text{ s}$. The maximum bubble pressure method [23,24] (Model EP-03, Kyowa Interface Science Co. Ltd., Saitama, Japan) and the standard Wilhelmy method [24] were used to measure the interfacial tension depending on the concentration of camphoric acid and pH.

3. Results

3.1. pH-dependent characteristic self-motion of a camphoric acid boat

Fig. 1 shows the time variation of the velocity and the acceleration of a camphoric acid boat at (a) pH 4.2, (b) pH 7.0, and (c) pH 10.0. At pH 4.0, the camphoric acid boat was initially accelerated and then the velocity reached to a fairly constant value. The reached constant velocity depended on the weight of the camphoric acid boat, as indicated in Fig. 1(a–1–3). The intermittent motion (repetition between motion and rest) was observed in Fig. 1(b and c). Fig. 2 shows the period of the intermittence (T_{inter}) depending on the pH of the aqueous phase. T_{inter} increased with the increase in pH between pH 6 and 10. The velocity of the self-motion was almost constant at pH lower than pH 6 ($T_{\text{inter}} = 0$) and was 0 at pH higher than pH 10 (no motion).

Fig. 3 shows the snapshots of the diffusion of the camphoric acid layer at the aqueous phase, the velocity of the camphoric acid boat, and the surface area of the camphoric acid layer at (a) pH 4.0 and (b) pH 7.0. CaSO_4 powder was used for visualizing the nature of the diffusion of the camphoric acid layer, i.e. the black and white parts

correspond to aqueous surfaces with and without the camphoric acid layer. The surface area of the surface active layer was large when the velocity of the camphoric acid boat was high. No camphoric acid layer was observed at pH 12 (the region of no self-motion).

3.2. Change of surface tension with pH of aqueous phase

Fig. 4 shows the surface tension depending on the concentration of camphoric acid at the

aqueous phases buffered at the different pH (4.2, 7.0, 10.0, and 11.9) by means of the maximum bubble pressure method. The concentration dependencies of the surface tension were characteristically varied among these samples with different pH. At pH 11.9, the surface tension was almost independent of the concentration of camphoric acid aqueous solution. At pH 4.2, the surface tension clearly decreased with the increase in the concentration of camphoric acid. At pH 7.0 and 10.0, the surface tension did not varied up to 20 and 35 mM, respectively, but markedly decreased

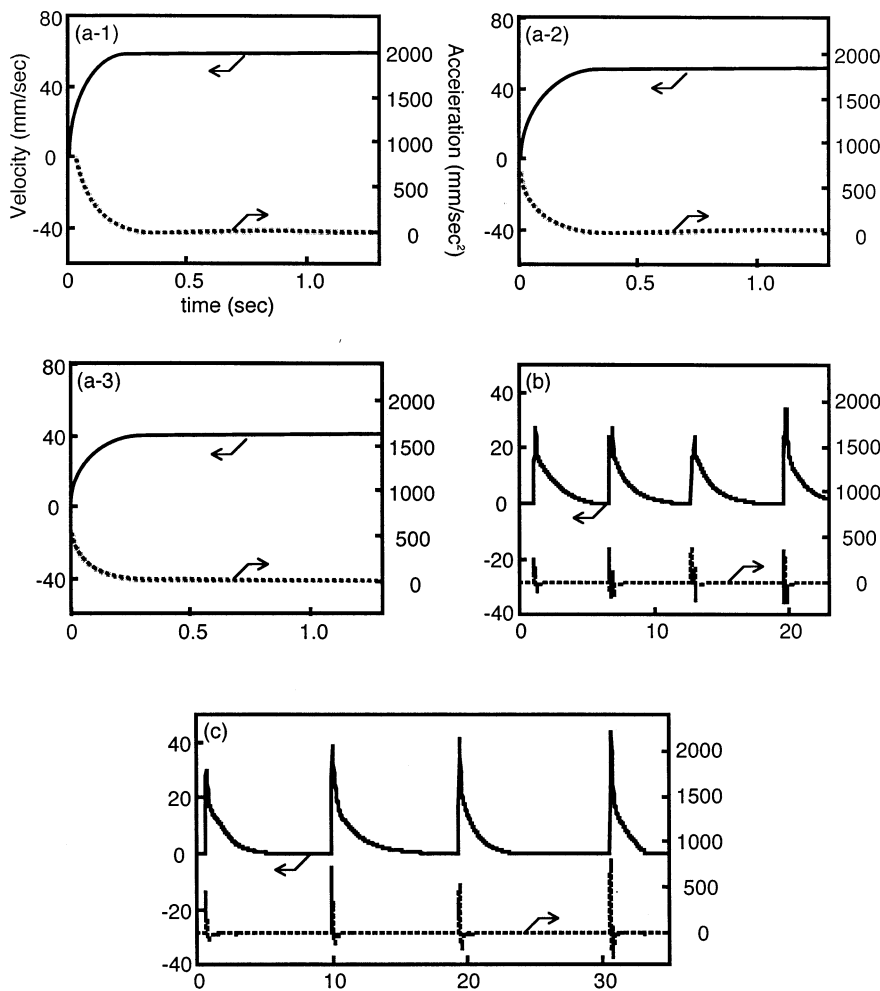


Fig. 1. Time variation of the velocity (solid line) and the acceleration (dotted line) of a camphoric acid boat on phosphate buffer solutions with different pH ((a) 4.2, (b) 7.0, and (c) 10.0). The mass of the camphoric acid boats were 3 mg (a-1, b, c), 5 mg (a-2), and 7 mg (a-3).

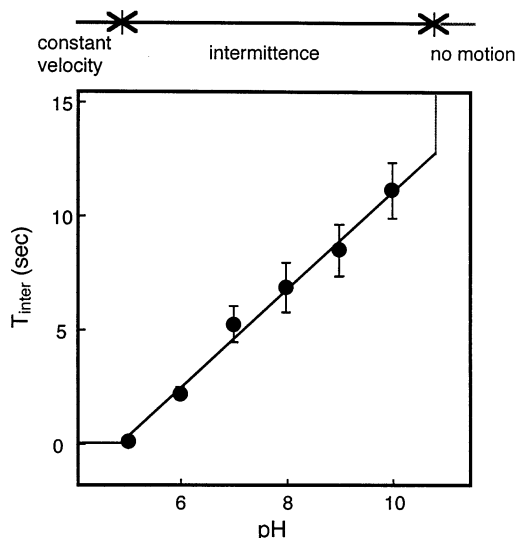


Fig. 2. Period of the intermittence (T_{inter}) depending on the pH of the aqueous phase. The mass of the camphoric acid boat was 3 mg. Analyzed data correspond to those in Fig. 1(b and c).

above these concentrations, respectively. In this measurement, the dependence of the surface tension on the rate of the interface creation was rarely observed probably due to its fast adsorption on the aqueous surface, therefore, the same dependencies of the surface tension on the concentration of camphoric acid solutions were also obtained by means of the Wilhelmy method.

Fig. 5 shows the temporal change in the tension (mN) between the camphoric acid scraping crystallized on the platinum wire (diameter, 0.5 mm) and the aqueous phase with the different pH ((a) 4.0, (b) 7.0, (c) 10.0, and (d) 11.9). In this measurement, a camphoric acid scraping crystallized on the platinum wire (circumference, ca. 4 mm) was come in contact with the aqueous surface (see Fig. 5), therefore, the decrease in the weight of the scraping due to its dissolution into the aqueous phase was added to the change in the surface tension. At pH 4.0, the surface tension was monotonously decreased with time. The periodic changes in the surface tension were observed at pH 7.0 and 10.0.

4. Discussion

4.1. Estimation of the driving force of the self-motion

At first, we evaluate the driving force of the self-motion, according to our previous papers [19,22] and referring to argument by Shanahan [16]. The motion of the camphoric acid boat may be described by the Eq. (1).

$$\frac{m}{dt} dv = FL - \eta mv \quad (1)$$

where m (kg) denotes the weight of the camphoric acid boat, v (m s^{-1}) the velocity of translational motion of the boat, F (N m^{-1}) the driving force of the self-motion, L (m) the contact length between the camphoric acid scraping and the aqueous surface, and η (s^{-1}) is the coefficient of viscosity on the viscous drag between a camphoric acid boat and an aqueous surface according to the Stokes' law. When $dv/dt = 0$, i.e. the camphoric acid boat moves with a constant velocity at pH 4, Eq. (2) holds.

$$FL = \eta mv_c \quad (2)$$

where, v_c (m s^{-1}) denotes the translational velocity of the camphoric acid boat at $dv/dt = 0$. Indeed, mv_c was experimentally almost constant at $(2.5 \pm 0.4) \times 10^{-7}$ (kg m s^{-1}).

Eqs. (3) and (4) are derived from Eqs. (1) and (2).

$$\frac{dv}{dt} = \eta(v_c - v) \quad (3)$$

$$\frac{m}{dt} dv = FL \left(1 - \frac{v}{v_c}\right) \quad (4)$$

Eq. (3) suggests that η is obtained from the relationship between dv/dt and $v_c - v$. Eq. (4) suggests that F is obtained from the relationship between $m dv/dt$ and $L(1 - v/v_c)$. Indeed, dv/dt was almost proportional to $v_c - v$ and η was obtained as 17.5 (s^{-1}) from the slope of line in Fig. 6(a). F at pH 4.0 was obtained as 2 (mN m^{-1}) from the slope of line in Fig. 6(b).

The driving force on the intermittent motion is estimated by Eq. (5).

$$F = m \frac{(dv/dt + \eta v)}{L} \quad (5)$$

Fig. 7 shows the time trace of F calculated based on the experimental data (Fig. 1(b and c)) and the Eq. (5) for (a) pH 7.0 and (b) pH 10.0. The maximum driving forces for pH 7.0 and 10.0 were estimated as 2 and 3.5 mN m⁻¹, respectively.

4.2. Mechanism of the characteristic self-motions depending on pH

We discuss the mechanism of the characteristic self-motions depending on pH based on the above results. Fig. 3 and the absence of camphoric acid

layer at pH 12 suggest that the surface area of the surface active layer was related to the velocity of the camphoric acid boat. The self-motion with a constant velocity at pH 4 suggests that the gradient of the surface tension around the boat is maintained. Although we have not succeeded to visualize the surface concentration of the camphoric acid layer yet, we previously reported that the surface pressure is decreased with the distance from the camphor scraping by using the Wilhelmy method [20].

The strong concentration-dependence of the surface tension at pH 4 suggests that the gradient of surface tension can be easily obtained as the driving force of the self-motion, as indicated in

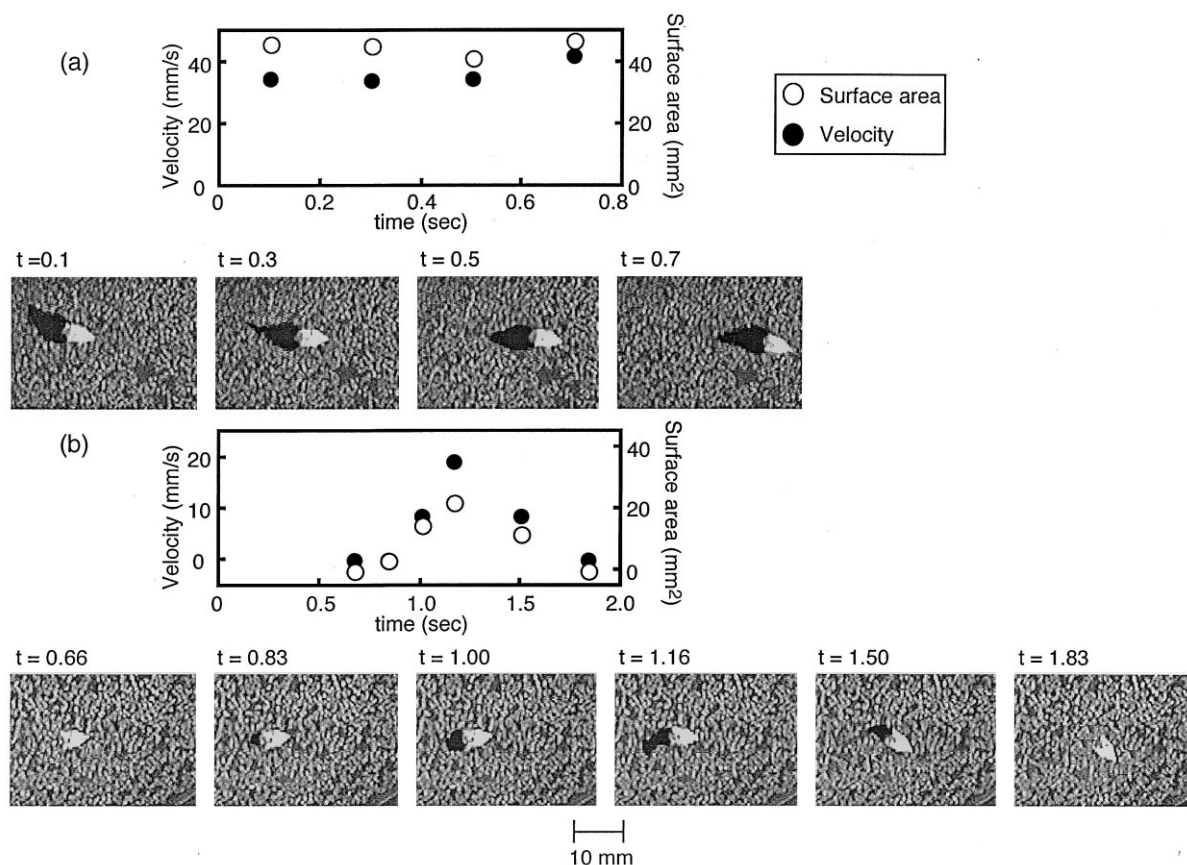


Fig. 3. Snapshots of the diffusion of the camphoric acid layer at the aqueous phase, the velocity of the camphoric acid boat (mass 3 mg), and the surface area of the camphoric acid layer at (a) pH 4.0 and (b) pH 7.0 (top view). CaSO₄ powder was spread over the aqueous surface before the placement of camphoric acid. The black and white parts correspond to aqueous surfaces with and without the camphoric acid layer.

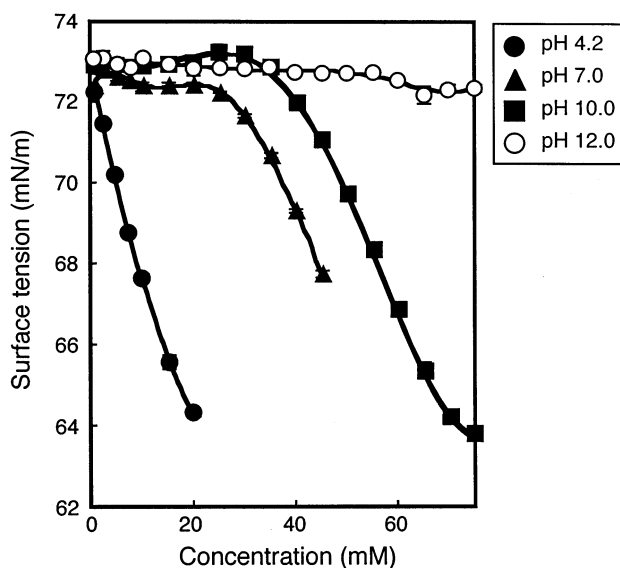


Fig. 4. Dependence of the surface tension on the concentration of camphoric acid in the aqueous phases buffered at the different pH (4.2 (closed circle), 7.0 (closed triangle), 10.0 (closed square), and 11.9 (open circle)) by means of the maximum bubble pressure method.

Fig. 4. As for the aqueous phase buffered at pH 11.9, the camphoric acid molecules adsorbed on the aqueous surface will not be surface active, as shown in Figs. 4 and 5. The independence of the surface tension suggests that the driving force can not be obtained, and then the camphoric acid boat does not move at pH 11.9.

As for the aqueous phase buffered at pH 7.0, the camphoric acid scraping can form the camphor layer and increase its surface concentration. However, the surface tension does not change up to the critical surface concentration in 20 mM camphoric acid solution, as seen in Fig. 4. In this stage, the driving force for the self-motion is not obtained up to the critical concentration. When the camphoric acid layer accumulates at the air–aqueous interface and then the surface concentration is over the critical value, the surface tension markedly decreases and then the driving force of the self-motion can be obtained. Thus the camphoric acid boat abruptly moved. The existence of the critical concentration has also been discussed on the other membrane systems, which indicate oscillatory phenomena [25–27].

A camphoric acid molecule has three states in an aqueous solution, i.e. $R-(COOH)_2$, $R-(COOH)(COO^-)$, and $R-(COO^-)_2$, where $R = C_8H_{14}$. pK_{a1} and pK_{a2} for camphoric acid are 4.57 and 5.10, respectively [28]. As for 60 mM camphoric acid solution at pH 12.0, $C_{R-(COOH)_2}$, $C_{R-(COOH)(COO^-)}$, and $C_{R-(COO^-)_2}$ are 4.45×10^{-16} , 9.48×10^{-9} , and $5.99999991 \times 10^{-2}$ M, respectively. Here, $C_{R-(COOH)_2}$, $C_{R-(COOH)(COO^-)}$, and $C_{R-(COO^-)_2}$ denote the concentrations of $R-(COOH)_2$, $R-(COOH)(COO^-)$, and $R-(COO^-)_2$, respectively. These values suggest that $R-(COO^-)_2$ is not surface active, as seen in Figs. 4 and 5. On the other hand, $C_{R-(COOH)_2}$, $C_{R-(COOH)(COO^-)}$, and $C_{R-(COO^-)_2}$ for 20 mM camphoric acid solutions at pH 10.0 are 9.36×10^{-13} , 2.52×10^{-7} , and 1.99997×10^{-2} M for 20 mM, and those for 60 mM are three times those for 20 mM, respectively. These values suggest that the adsorption constants of $R-(COOH)_2$ and $R-(COOH)(COO^-)$, which is surface active, on the air–water interface are markedly larger than another one and that the aggregates among three components of camphoric acid molecules induces a phase transition at the critical concentration, as seen in Fig. 4.

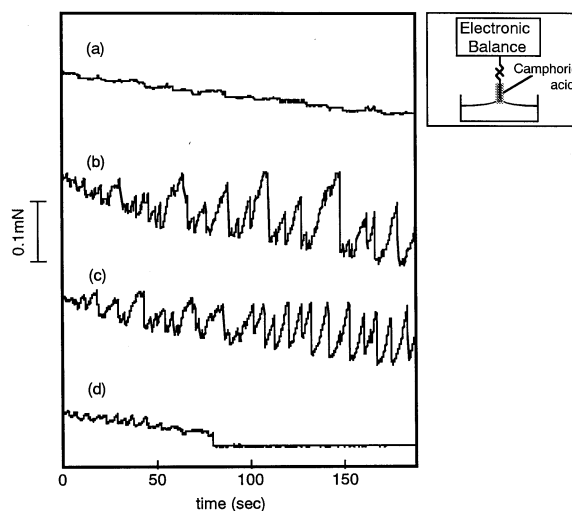


Fig. 5. Time trace of the tension (mN) between the camphoric acid scraping crystallized on the platinum wire and the surface of the phosphate buffer solutions of various pH ((a) 4.0, (b) 7.0, (c) 10.0, and (d) 11.9). At $t = 0$, the camphoric acid crystal was touched with the aqueous phase.

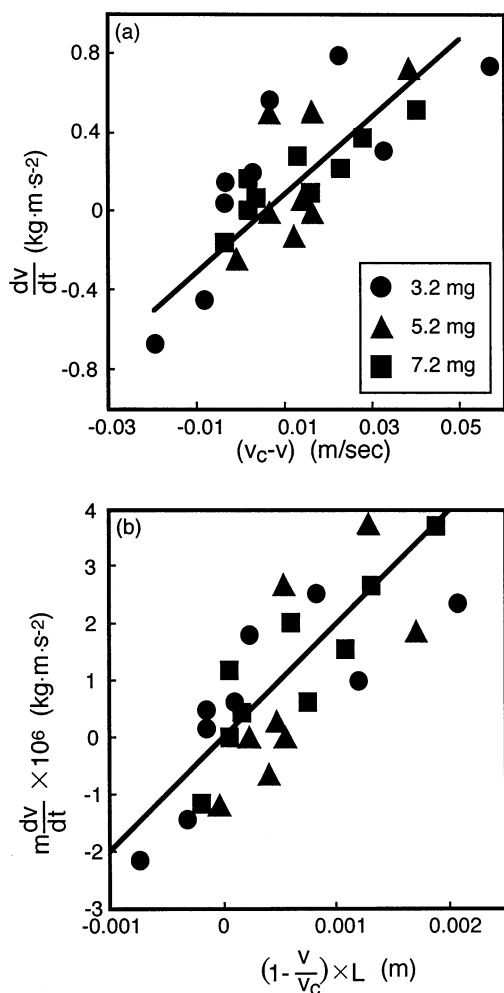


Fig. 6. The plot of (a) dv/dt vs. $v_c - v$ and (b) $m dv/dt$ vs. $L(1 - v/v_c)$. The data correspond to those in Fig. 1(a). The mass (mg) in Figure is the weight of the camphoric acid boat ((closed circle) 3 mg, (closed triangle) 5 mg, and (closed square) 7 mg).

Since the self-motion of the camphoric acid boat can move itself to the pure aqueous surface, the camphoric acid boat does not move until the concentration of the camphoric acid layer reaches the critical value. Thus, the periodic intermittent motion can be repeated based on the above process, as seen in Figs. 1–3. As for the pH 10.0, the period of the intermittent motion was longer than that at pH 7.0 (Figs. 1 and 2). This result is

reflected to the fact that the critical concentration at pH 7.0 (20 mM camphoric acid solution) is higher than that at pH 10.0 (35 mM), i.e. the time taken to reach the critical value at pH 10.0 is longer than that at pH 7.0.

As radius of van der Waals radius, r , was calculated to be 4.83 Å, the 2-dimensional size (πr^2) of the camphoric acid molecule was ca. 73 Å². Here, this value was calculated by the ab initio calculation and the restricted Hartree–Fock wave function with the STO-3G basis set was used for geometry optimization. From the slope of the curve in Fig. 4 and the Gibb's adsorption isotherm, the occupied surface area of a camphoric acid molecule was obtained to be 152 and 44 Å² at 10 mM and pH 4.2 and 60 mM and pH 10.0, respectively. These calculations suggest that the surface active camphoric acid layer is composed with a high density and the occupied surface area of camphoric acid may be a relevant factor on the dramatic pH dependence of the self-motion.

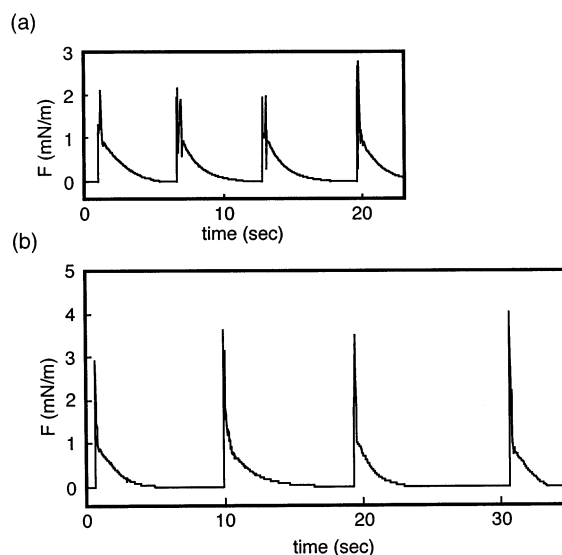


Fig. 7. Time trace of F calculated by using the experimental data and the Eq. (5) for (a) pH 7.0 and (b) pH 10.0. τ was used as 17.5 (s⁻¹) from the slope of line in Fig. 6(a). L was used as 2 (mm) from the actual experiments. Analyzed data for (a) and (b) correspond to those in Fig. 1(b and c), respectively.

5. Conclusion

The characteristic spontaneous motions depending on pH may be induced by a change in the state of camphoric acid layer, which is related to the surface tension depending on the concentration and pH. In this paper, we have discussed that the driving force is related to the gradient in the surface tension. However, the hydrodynamic effects (short time scale and extraneous inertia at start of experiment) should be addressed as the driving force in addition to the effect of surface tension in the future studies. In addition, a solutocapillary effect (or solute-Marangoni effect) which involves surface convection from low to high surface tension, should be taken into account as the important factor on the camphor motion in addition to the effect of the gradient in the surface tension [17,18].

According to the Curie–Prigogine theorem, scalar variables cannot couple with vector values under isotropic conditions [29–31]. This implies that chemo-mechanical transducer can create under anisotropic conditions. In this experiment, the direction of the self-motion is determined by the manner of attachment of camphoric acid scraping to the plastic boat, i.e. the symmetric diffusion of camphoric acid layer around the scraping is broken by the plastic boat. The present study suggests that one may create various manners of self-motion which is sensitive to the environment and control their vector if one can model surface active substances which indicate characteristic curves on the concentration versus surface tension and one can introduce the heterogeneous conditions.

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