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**Title**

Chemosensitive running droplet

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Chemosensitive running droplet

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Chemical control of the spontaneous motion of a reactive oil droplet moving on a glass substrate under an aqueous phase is reported. Experimental results show that the self-motion of an oil droplet is confined on an acid-treated glass surface. The transient behavior of oil-droplet motion is also observed with a high-speed video camera. A mathematical model that incorporates the effect of the glass surface charge is built based on the experimental observation of oil-droplet motion. A numerical simulation of this mathematical model reproduced the essential features concerning confinement of oil droplet motion within a certain chemical territory and also its transient behavior. Our results may shed light on physical aspects of reactive spreading and a chemotaxis in living things.

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I. INTRODUCTION

The spontaneous motion of reactive droplets has attracted considerable attention in relation to energy transduction by living organisms—i.e., chemomechanical energy transduction. In 1978, the motion of a droplet driven by a surfacetension gradient was predicted by Greenspan to explain some aspects of cell cleaving from a physicochemical viewpoint [1]. Various kinds of droplet motion driven by a surfacetension gradient have been reported since then, where the surface-tension gradient was given by an initial [2,3] or an external [4] asymmetry in a surface condition. Spontaneous motion in reactive spreading, or a droplet driven by a self-produced surface-tension gradient, has also been noted in various experimental systems [5–13]—for example, a droplet of surfactant on a gold surface [5], alloy melting [6], and a water droplet containing silane on a glass substrate [7–9]. To interpret these phenomena, extensive theoretical studies of reactive droplets have been performed with the lubrication approximation [14–16].

An oil-water system composed of an organic phase with potassium iodide and iodine and an aqueous phase containing stearyl trimethyl ammonium chloride (STAC) exhibits self-agitation at the oil-water interface, accompanied by spatiotemporal instability of interfacial tension [17–22]. It has also been found that the motion of an oil droplet in an oil-water system exhibits chemosensitivity [23]. Based on the measurement of the electrical potential at the oil-water interface in a similar system, the nature of the electrical fluctuation and oscillation has been shown to strongly depend on the chemical properties and the concentration [24]. However, the detailed mechanism of this effect of chemical substances has not yet been clarified. Recently, it was proposed that an oil-water system also shows reactive spreading on a glass surface with recovery of the surface condition [25,26].

In the present study, we experimentally observed the chemosensitive motion of an oil droplet on a glass substrate that had been partially pretreated with acid. We found that an oil droplet exhibits various behaviors, such as turning-back motion, stopping at a certain position, or slowing down around regions treated with acid. In addition, we also noted that the velocity and shape of the oil droplet show damped oscillation while the droplet moves continuously. However, detailed observations show that the motion of an oil droplet strongly depends on slight changes in the surface condition of the substrate. In terms of the argument given in our previous study [26], we expect that the chemosensitivity of oil-droplet motion is caused by the condition of the glass surface affected by acid, which inhibits the aggregation of stearyl trimethyl ammonium ion (STAC+ ion) on the glass surface. To confirm this hypothesis, we idealize an oil droplet as self-propelling spring beads whose driving force is given by the
In the experiments on an acid-treated narrow glass substrate, the glass substrate (1 mm × 52 mm × 3.1–3.2 mm) was cut from slide glass. Both ends of this substrate were pretreated with acid for 15 mm [Fig. 1(b)]. An oil droplet of 15 μl was placed on the substrate in the same manner as in the Y-shaped path experiment. The motion of an oil droplet was recorded by a high-speed video camera (RedLake MASD Inc., San Diego, CA; Motion Scope PCI) at 125 frames per second. All measurements were carried out at room temperature (20 °C ± 3 °C). The recording of a droplet motion was digitized by an image-processing system (Library, Tokyo).

III. RESULTS

The spontaneous motion of an oil droplet was found to be confined within a Y-shaped path and a narrow substrate (Figs. 2 and 3). On the Y-shaped path [Fig. 2(a)], motion is clearly limited to within the region that was not treated with acids. On the narrow substrate, oil droplets exhibit quasi-one-dimensional motion [26]; i.e., an oil droplet of 15 μl showed turning-back motion that resulted in a shuttling motion [Figs. 2(b) and 2(c)] when the oil droplet could not intrude into the acid-treated region. The time traces of oil-droplet velocity \(v\) and the apparent length of an oil droplet \(r\) in the motion shown in Fig. 2(b) are plotted in Fig. 4. \(v\) and \(r\) showed damped oscillation after each returning motion until both reached steady values. On the other hand, when an oil droplet of 15 μl intruded into the acid-treated region, the oil droplet stopped and stood still [Fig. 3(a)] or slowed down [Fig. 3(b)]. The motion of an oil droplet was found to be sensitively dependent on the manner of acid treatment.

IV. DISCUSSION

It has been suggested by our previous study [26] that the motion of an oil droplet can be explained in terms of reactive spreading [15]. STA⁺ ions in the aqueous phase aggregate on the glass surface that has negative charges at neutral pH [29]. The organic phase dissolves STA⁺ ions that have adhered to the glass substrate, and this dissolution is promoted since STA⁺ and \(I_3^-\) in the organic phase make an ion pair. The ion pair dissolves well in nonpolar solvent—i.e., the organic phase. Therefore, a difference in interfacial energy arises from the difference in the concentration of STA⁺ ions on the glass surface between the front and back of an oil droplet (Fig. 5), and the oil droplet is driven by Marangoni effect. Thus, the condition of the glass surface on which STA⁺ ions aggregate plays an important role in the motion of an oil droplet.

Nakata and co-workers examined the chemosensitivity of the motion of an oil droplet escaping from acids [23]. In their experiment, hydrochloric acid was injected in the aqueous phase while an oil droplet was moving. From the above discussion, modification of a glass surface by acids significantly affects oil-droplet motion. It has been reported that the point of zero charge \((pH_\text{pzc})\) of the SiO₂ surface is around 2.2 [30,31]. Thus, the glass surface charge may have been partially reversed to be positive due to the effect of acid since
the pH of 1 M sulfuric acid is around 0. We can consider that
this results in fewer adsorption sites for STA⁺ ions on the
glass surface. This may explain why an oil droplet showed
confined motion when it was encircled by an acid-treated surface. Furthermore, the dependence of droplet motion on the condition of the acid-treated region can be attributed to the difference in the number of adsorption sites on the glass surface. To explain the various motions of an oil droplet, it seems appropriate to control the surface condition of a glass substrate much more accurately. On the other hand, in the experimental process, these different types of the characteristic motions were observed even under nearly identical conditions, including the concentration and duration of treatment with sulfuric acid. To understand this strong dependence on the condition of the glass surface, we constructed a mathematical model and conducted a numerical simulation of oil-droplet motion on a narrow substrate.

There may be various ways to theoretically analyze for the spontaneous motion of an oil droplet, such as interface dynamics based on Young’s equation [14,15] or a hydrodynamic approach which adopts the lubrication approximation [16]. Instead of making a detailed model, we propose a simple “beads-spring” model for an oil droplet to abstract the essential features of droplet motion.
The concentration of STA\(^+\) ions on the glass surface is set as a hydrophilic head. The characteristic size of the oil droplet, respectively.

V. MODELING

Since we want to know the basic mechanism of the motion of an oil droplet on a glass substrate, we make a simple one-dimensional model. The \(x\) axis is set along the surface of the glass substrate. The droplet proceeds on a line with stretching and shrinking. The positions at the both ends of the droplet are set as \(x_1(t)\) and \(x_2(t)\), where \(x_1 < x_2\). The concentration of STA\(^+\) ions on the glass surface is set as \(u(x,t)\).

The dynamics of \(x_1\) and \(x_2\) are written as follows:

\[
\frac{d^2 x_1}{d t^2} = -\mu_0 \frac{d x_1}{d t} - \frac{\partial E}{\partial x} \bigg|_{x=x_1} - \beta(r_0)(x_1(t) - x_2(t) - r_0),
\]

\[
\frac{d^2 x_2}{d t^2} = -\mu_0 \frac{d x_2}{d t} - \frac{\partial E}{\partial x} \bigg|_{x=x_2} - \beta(r_0)(x_2(t) - x_1(t) + r_0),
\]

where \(\sigma\), \(\mu_0\), and \(r_0\) correspond to the mass of the oil droplet reduced to two lines, a viscous damping coefficient, and the characteristic size of the oil droplet, respectively. \(\beta(r_0)\) is the elastic constant of the oil droplet with characteristic size \(r_0\) (see Appendix A):

\[
\beta(r_0) = \frac{2\gamma w}{r_0}.
\]

\(E(u)\) is the surface energy of the glass surface modulated by the STA\(^+\) ions adsorbed on it:

\[
E(u) = \frac{e_0}{1 + au^n},
\]

where \(e_0\), \(a\), and \(n\) are positive constants. On the other hand, the dynamics of \(u\) can be written as follows:

\[
\frac{d^2 x}{d t^2} = \frac{\partial^2 u}{\partial x^2} + F(x,t),
\]

where \(F(x,t)\) corresponds to the desorption of STA\(^+\) ions from the glass surface to the oil droplet. For this term, we assume the following description:

\[
F(x,t) = \begin{cases} -k_1 u, & x_2(t) < x < x_1(t), \\ k_2(u_0 - u), & x_0 < x < x_2(t), \\ k_3(u_1 - u), & 0 < x < x_1(t), \\ 0, & x < x_1(t) \end{cases},
\]

where \(k_1\), \(k_2\), \(u_0\), \(\ell\), and \(\ell_0\) are positive constants that correspond to the desorption rate, the adsorption rate, the saturated concentration of STA\(^+\) ions on the glass surface, the length of the glass substrate, and the length of the glass substrate treated with acid, respectively (see Fig. 6 and Appendix B). The initial and boundary conditions are set as

\[
\frac{\partial u}{\partial x}(t,0) = \frac{\partial u}{\partial x}(t,\ell) = 0,
\]

\[
u(t,x) = \begin{cases} u_0, & x_0 < x < x_1(t), \\ u_1, & 0 < x < x_0, \ell - \ell_0 < x < \ell, \\ x_1(t), & x_2(t) = x_2(t) < x_1(t), \\ 0, & x < x_1(t), \ell - \ell_0 < x < \ell, \\ \end{cases},
\]

\[
\frac{d x_1}{d t}(0) = \frac{d x_2}{d t}(0) = 0.
\]

To normalize Eqs. (1)–(9), we introduce the following dimensionless variables:

\[
U = \frac{u}{u_0}, \quad X_1(x) = \frac{x_1}{\ell}, \quad X_2(x) = \frac{x_2}{\ell}, \quad X = \frac{x}{\ell}, \quad T = k_1 t.
\]

We then derive the following dimensionless system from Eqs. (1)–(9):

\[
\frac{d^2 X_1}{d T^2} = \frac{\partial^2 U}{\partial X^2} + F(U,X_1,X_2; \ell_0).
\]
\[ \frac{d^2X_1}{dT^2} = -\mu \frac{dX_1}{dT} - \frac{\partial E}{\partial X} \bigg|_{X=X_1} - B(R_0)[X_1(T) - X_2(T) - R_0], \]

\[ \frac{d^2X_2}{dT^2} = -\mu \frac{dX_2}{dT} - \frac{\partial E}{\partial X} \bigg|_{X=X_2} - B(R_0)[X_2(T) - X_1(T) + R_0], \]

\[ E(U) = \frac{E_0}{1 + A U^n}, \]

\[ \frac{\partial U}{\partial T} = D \frac{\partial^2 U}{\partial X^2} + F(U,X,X_1(T),X_2(T);L_0), \]

\[ F(U,X,X_1(T),X_2(T);L_0) = \begin{cases} -U, & X_2(T) \leq X \leq X_1(T), \\ K_2(U_0 - U), & L_0 \leq X < X_2(T), X_1(T) < X < 1 - L_0, \\ K_3(U_1 - U), & 0 < X \leq L_0, 1 - L_0 \leq X < 1, \end{cases} \]

with the initial and boundary conditions

\[ \frac{\partial U}{\partial X}(T,0) = \frac{\partial U}{\partial X}(T,1) = 0, \]

\[ U(0,X) = \begin{cases} 1, & L_0 < X < 1 - L_0, \\ U_1, & 0 < X \leq L_0, 1 - L_0 \leq X < 1, \end{cases} \]

\[ X_1(0) = X_{10}, \quad X_2(0) = X_{20}(<X_{10}), \]

\[ \frac{dX_1}{dT}(0) = \frac{dX_2}{dT}(0) = 0, \]

where

\[ \mu = \frac{\mu_0}{\sigma k_1}, \quad E_0 = \frac{e_0}{\ell \sigma k_1}, \quad R_0 = \frac{r_0}{\ell}, \]

\[ B(R_0) = \frac{\ell^2 (r_0)}{\sigma k_1^2} = \frac{W}{R_0}, \quad W = \frac{2 \gamma \nu \ell}{\sigma k_1}, \quad A = au_0^n, \]

\[ D = \frac{d}{k_1 \ell^2}, \quad K_2 = \frac{k_2}{k_1}, \quad K_3 = \frac{k_3}{k_1}, \quad U_1 = \frac{u_1}{u_0}, \quad U_0 = \frac{u_0}{u_0}, \]

\[ L_0 = \frac{L_o}{\ell} (<1), \quad X_{10} = \frac{x_{10}}{\ell}, \quad X_{20} = \frac{x_{20}}{\ell}. \]

**VI. NUMERICAL RESULTS**

We performed a numerical simulation using Eqs. (11)–(15) under the initial and boundary conditions shown in Eqs. (16)–(18).

![FIG. 7. Spatiotemporal plot of the oscillatory motion of a droplet given by numerical calculations using Eqs. (11)–(18). Only the parameter \( U_1 \) was changed: (a) \( U_1=0.65 \) and (b) \( U_1=0.658 \). The other parameters are \( \mu=0.2, \ R_0=0.05, \ E_0=5 \times 10^{-5}, \ A=1, \ n=4, \ W=0.1, \ D=2.5 \times 10^{-5}, \ L_0=0.25, \ U_0=1, \ K_2=1, \ K_3=1, \ X_{10}=0.23, \) and \( X_{20}=0.27 \). The thick lines along the \( x \) axis correspond to the regions treated with acid.](image)

We only changed the parameter \( U_1 \), while all of the other parameters are fixed. It is noted that \( U_1 \) corresponds to the saturated concentration at the region treated by acid. Spatiotemporal plots of the droplet given by the numerical calculations are shown in Figs. 7 and 8.

When \( U_1 \) is small enough—i.e., when it is difficult for STA* ions to adsorb to the acid-treated region—the oil droplet moves back and forth inside the untreated region, as shown in Fig. 7(a). As \( U_1 \) increases slightly, the oil droplet does not turn back quickly but rather rests at the border between the acid-treated region and the untreated region. After a brief stop, it begins to move backward, and this intermittent shuttling motion is repeated as shown in Fig. 7(b). For much larger \( U_1 \), the oil droplet does not go back any more, as shown in Fig. 8. The oil droplet goes into the acid-treated region, and it continues to move very slowly or stops according to the value of \( U_1 \).

These differences in the characteristics of the motion of an oil droplet are seen only with slight differences in \( U_1 \). Thus, the numerical results suggest that a slight fluctuation in acid treatment can cause a dramatic change in the character-
istics of the motion of an oil droplet. In the experiments, the oscillatory motion shown in Fig. 2, the stopping of the droplet at the border shown in Fig. 3, and the slow motion in the acid-treated region shown in Fig. 3 were observed under almost the same conditions. We can guess that the various kinds of motion observed in the experiments are due to slight differences in the acid treatment of the glass.

We have also noted that intermittent-oscillatory motion and stopping does not appear without a diffusion term in Eq. 5. This suggests that the diffusion on a glass surface has a significant effect in the real experimental system. There have been several studies concerning the effect of diffusion on the motion of a self-running droplet [16,32,33]. Thiele et al. [16] stated that in their model a running droplet can be stopped by increasing the effect of a surfactant diffusion on a substrate. In our study, the diffusion of surfactant on the glass substrate is not large enough to stop the motion of a droplet. However, at the boundary of the acid-treated region where an oil droplet stopped, the concentration of the surfactant on the acid-treated region is in equilibrium with the diffused surfactant from the nontreated region. Thus, the effect of diffusion is optimized by the inhomogeneity in the glass surface so that an oil droplet stops its motion.

Figure 9 shows (a) the normalized length and (b) the velocity of an oil droplet. When the velocity of the oil droplet is large, the length of the droplet increases and vice versa, which corresponds well to the actual experimental trend (Fig. 4).

VII. CONCLUSION

In the present study, we investigated the self-running motion of an oil droplet on an acid-treated glass substrate. In these experiments, the oil droplet undergoes either oscillatory motion within the untreated region or stopping and slowing at the border between the acid-treated region and the untreated region. We made a simple “beads-spring” model and performed numerical calculations, which suggest that a slight difference in the nature of adsorption in the acid-treated region can cause a dramatic change in the characteristics of this motion. The numerical results reproduced well the experimental results. In particular, the numerical results suggest that a slight difference in acid treatment can cause a dramatic change in the motion of an oil droplet. The results with the model also suggest that diffusion on the glass surface plays an important role in the spontaneous motion of a droplet. The inhomogeneity of the glass surface—i.e., the boundary of the surface condition—optimizes the effect of diffusion.

In this study, an oil droplet avoided the area that was treated with acid. It is possible that some other chemicals may attract an oil droplet. Above all, the present results...
mass of the droplet, and
where $H_9253$ and height are
droplet is shaped as a rectangular solid, whose length, width,
an oil droplet. As shown in Fig. 10, we assume that the
minute variation in the chemical concentration in space by
showed that a running droplet senses information regarding a
FIG. 10. Schematic representation of the framework of the
“beads-spring” model. The hemisphere-shaped oil droplet as shown
in (a) is regarded as a rectangular solid. Since we consider only the
x dimension, the conservation law for the volume corresponds to
the elastic constant of the spring.

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APPENDIX A: VALIDITY OF THE BEADS-SPRING
MODEL

We discuss here the validity of the beads-spring model for
an oil droplet. As shown in Fig. 10, we assume that the
droplet is shaped as a rectangular solid, whose length, width,
and height are $r, w,$ and $h$, respectively. The volume of the
droplet is conserved:

$$V = rwh.$$  \hspace{1cm} (A1)

The main terms of the energy of the droplet are due to
gravity and interfacial tension:

$$F = \frac{1}{2} mgh + \gamma \left[ rw + 2hw + 2rh \right]$$
$$= -\frac{\rho V^2 g}{2rw} + \gamma \left[ rw + 2V \left( \frac{1}{r} + \frac{1}{w} \right) \right],$$  \hspace{1cm} (A2)

where $\gamma$ is the interfacial tension, $\rho$ is the density, $m$ is the
mass of the droplet, and $g$ is the gravitational acceleration.

First, we calculate the fixed point. At the fixed point,
$\frac{dF}{dr}=0$; therefore,

$$\frac{dF}{dr} = -\frac{\rho V^2 g}{2rw} + \gamma \left[ w - \frac{2V}{r^2} \right] = 0,$$  \hspace{1cm} (A3)

which gives the fixed point $r_0$:

$$r_0 = \left( \frac{\rho V^2 g}{2\gamma w^2} + \frac{2V}{w} \right)^{1/2}.$$  \hspace{1cm} (A4)

The elastic constant $\beta(r_0)$ is given as

$$\beta(r_0) = \frac{d^2F}{dr^2} \bigg|_{r=r_0} = \frac{2\gamma w}{r_0}.$$  \hspace{1cm} (A5)

From the above discussion, we can regard the oil droplet
as two beads connected with a spring whose elastic constant
is proportional to the inverse of the characteristic size of the
droplet.

The spring constant is on the same order of magnitude
even if the shape of the droplet is regarded as a caplike or
ribbon-shaped droplet.

APPENDIX B: MODEL OF THE ADSORPTION-
DESORPTION PROCESS ON A GLASS SURFACE

The effect of acids is thought to result in a decrease in the
number of adsorption sites $X_{\text{sur}}$ for $\text{STA}^+$ ions [29]. Assum-
ing that adsorption-desorption is a lamjuir isothermal pro-
cess,

$$\text{STA}^+ + X_{\text{sur}}^- = \text{STAX}_{\text{sur}}^-.$$  \hspace{1cm} (B1)

Since $m_0$ is the total density of adsorption sites on the glass
surface, $x$ is the density of free adsorption sites, and $u$ is the
concentration of $\text{STA}^+$ ion in the aqueous phase, the surface
concentration $u_{\text{sur}}$ of $\text{STAX}_{\text{sur}}$ under aqueous phase changes
according to

$$\frac{du_{\text{sur}}}{dt} = ku \left( x_0 - \frac{1 + \frac{u}{k}}{k u} \right) u_{\text{sur}},$$  \hspace{1cm} (B2)

where we assume that $x + u_{\text{sur}} = x_0$ and $k$ and $k^{-1}$ are reaction
constants in Eq. (B1). The effect of acid is included in the
decrease in $x_0$, which is equivalent to the decrease in $u_0$ to $u_1$
in the acid-treated region in Eq. (6).

Similarly, the desorption that occurs under the organic
phase is considered as,

$$\text{STAX}_{\text{sur}}^- + \text{I}_3^- \rightarrow \text{STAI}_3^- + X_{\text{sur}}^-.$$  \hspace{1cm} (B3)

We assume that the reaction proceeds only from left to right.
Therefore, $u_{\text{sur}}$ changes according to

$$\frac{du_{\text{sur}}}{dt} = -\tilde{k} u_{\text{sur}} v,$$  \hspace{1cm} (B4)

where $v$ represents the concentration of $\text{I}_3^-$ in an oil droplet
and $\tilde{k}$ represents the reaction constant. This equation, again,
is equivalent to Eq. (6).