Supporting Information for "Oscillation of Speed of a Self-Propelled Belousov– Zhabotinsky Droplet"

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1. Synchronization of speed with redox state

To clarify the relationship between the redox state and speed, a return map of the phase difference was constructed (Figure S1) where the phase difference was defined using the times of the peak in brightness ($t_b(n)$) and speed ($t_s(n)$) as follows:

$$\Delta\theta(n) = 2\pi \frac{t_s(n) - t_b(n)}{t_b(n+1) - t_b(n)}.$$
 (1)

This analysis indicates that the speed of the self-propelled motion is synchronized in phase with the redox state of the aqueous phase.



Figure S1. (a) Time series of the (solid black line) speed of the self-propelled motion and (broken blue line) brightness of the blue color, which indicates the redox state of the droplet. The inset images show the color change during oscillation. (b) Return map of the phase difference between the speed and brightness. This map indicates that the peak times of the speed have almost the same values as those of the brightness. The components of the BZ solution were $[BrO_3^-]$ (0.40 M), $[H_2SO_4]$ (0.60 M), $[CH_2(COOH)_2]$ (0.20 M), $[Br^-]$ (0.030 M), and $[Fe(phen)_3^{2+}]$ (2.0 mM). The diameter of the droplet was 690 µm.

2. Relationship between speed u and reaction rate κ_s

The amplitude equations for a self-propelled droplet driven by Marangoni flow has been reported.¹⁶ Using this theoretical approach, we can consider the relationship between the speed of the droplet and the reaction rate of a surfactant. The theoretical approach in Ref. 16 considered that the surfactant adsorbs on the oil/water interface and decomposes after characteristic time κ_s^{-1} . The interfacial tension is assumed to linearly decrease with the surface concentration of the adsorbed surfactant $\Gamma(\theta)$. The adsorption and decomposition of the surfactant generates inhomogeneity in the spatial distribution and induces Marangoni flow. Considering the above factors, Ref. 16 derived the following reaction–diffusion equation for surface concentration $\Gamma(\theta)$:

$$\frac{\partial \Gamma}{\partial t} + v_{\theta}(R) \nabla_{s} \Gamma = D_{s} \nabla_{s}^{2} \Gamma - \kappa_{s} \Gamma + \left[D_{o} \frac{\partial c}{\partial r} - D_{i} \frac{\partial c}{\partial r} \right]_{r=R},$$
(S1)

where v_{θ} is the θ component of the velocity field; *R* is the droplet size; D_{o} , D_{i} , and D_{s} are the diffusion constant for the outer, inner, and surface of the droplet, respectively; and *c* is the bulk concentration of the surfactant. In addition, Ref. 16 considered the reaction–diffusion equation for the bulk concentration of the surfactant where it focused only on the surfactant concentration in the outer fluid as follows:

$$\frac{\partial c}{\partial t} + v \cdot \nabla c = D \nabla^2 c - \kappa (c - c_\infty).$$
(S2)

The boundary conditions of this equation are the constant value c_{∞} at infinity and its proportion to surface concentration $\Gamma(\theta)$ at the interface. The proportional constant of $\Gamma(\theta)$ and $c(R,\theta)$ is α , which is the inverse of the Henry's constant. Reference 16 expanded surface concentration $\Gamma(\theta)$ using the Legendre polynomials and derived the amplitude equations by focusing only at n = 0and n = 1 modes where the speed of droplet motion u can be expressed as $u = u_1A_1$. Using a weak nonlinear analysis, Ref. 16 obtained the critical point of drift bifurcation u_1^* as follows {Eq. (21) in Ref. 16}:

$$u_1^* = \frac{2D_s/R^2 + \kappa_s + D\alpha/\lambda}{\Lambda_{12}(c_{\infty} - \alpha A_0)},$$
(S3)

where λ is the typical length scale to relax the surfactant concentration in the bulk (= $\sqrt{D/\kappa}$),

 A_{12} is the coefficient, and A_0 is the amplitude at n = 0 mode. For $R >> \lambda$, A_0 can be expressed as

$$A_0 \cong \frac{c_\infty}{\kappa_s \lambda / D + \alpha}.$$
 (S4)

In addition, Ref. 16 showed the steady-state velocity of the droplet *u* under the condition $\alpha \ll \kappa_s \lambda / D$ as follows {Eq. (22) in Ref. 16}:

$$u \cong u_0 \sqrt{1 - \frac{u_1^*}{u_1}},\tag{S5}$$

where $u_0 = \sqrt{D\kappa R/\lambda}$ for $R >> \lambda > 0.01 R$.

In our system, the surfactant reacts with Br₂, and the interfacial tension increases. Assuming that this chemical reaction is linear, the reaction rate can be expressed as $k_i[Br_2]\Gamma$. Thus, κ_s can be expressed as $k_i[Br_2]$ and is proportional to the Br₂ concentration. To clarify the relationship between *u* and κ_s , we focus on u_1^* because u_0 and u_1 are independent of κ_s . Using Eq. (S4), Eq. (S3) can be rewritten as a function of κ_s .

$$u_1^* = \frac{2D_s/R^2 + D\alpha/\lambda + \kappa_s}{\Lambda_{12}c_{\infty} \left(1 - \frac{D\alpha/\lambda}{\kappa_s}\right)} \equiv \frac{a + \kappa_s}{b\left(1 - \beta/\kappa_s\right)},$$
(S6)

where *a*, *b*, and β are constant. Figure S1 shows that u_1^* has a minimum value at $\kappa_s = \kappa_s^*$ ($\approx \sqrt{a\beta}$). Therefore, according to Eq. (S5), droplet speed *u* increases with κ_s (Figure S2b), *i.e.*, corresponding to the Br₂ concentration, for $D\alpha/\lambda \ll \kappa_s \ll \kappa_s^*$.



Figure S2. Plot of u_1^* and u/u_0 against κ_s . The parameters are a = 0.001, b = 0.001, and $\beta = 0.00001$.

3. Numerical calculation using the modified Oregonator model

The original version of the Oregonator is given by

$A + Y \rightarrow X + P$	(01)
$X + Y \rightarrow 2P$	(O2)
$A + X \rightarrow 2X + 2Z$	(03)

$$2X \rightarrow A + P \tag{O4}$$

$$Z \rightarrow fY$$
 (O5)

In addition to these chemical equations, the following chemical equations concerning Br_2 (= U) were considered:³⁶

$$P \rightarrow Y, \tag{O6}$$
$$Y + P \leftrightarrow U, \tag{O7}$$

$$U \rightarrow \text{atmosphere.}$$
 (O8)

Equation (O8) indicates the physical removal of Br_2 . In our BZ droplet system, instead of such physical removal process, the interfacial reaction of the surfactant (MO) with Br_2 was considered. Therefore, Eq. (O8) was replaced by the following interfacial chemical reaction:

$$U + MO \rightarrow Q.$$
 (O8)'

where MO is the surfactant and Q is the product of the interfacial chemical reaction. Based on these eight chemical equations, we developed ordinary differential equations for five variables, namely, X, Y, Z, P, and U.

$$\begin{aligned} \frac{dX}{dt} &= k_1 A Y - k_2 X Y + k_3 A X - 2k_4 X^2 \\ \frac{dY}{dt} &= -k_1 A Y - k_2 X Y + \frac{1}{2} f k_5 Z + k_6 P - k_7 Y P + k_{-7} U \\ \frac{dZ}{dt} &= 2k_3 A X - k_5 Z \\ \frac{dP}{dt} &= k_1 A Y + 2k_2 X Y + k_4 X^2 - k_6 P - k_7 Y P + k_{-7} U \\ \frac{dU}{dt} &= k_7 Y P - k_{-7} U - k_8 U \end{aligned}$$

We numerically calculated the above equations using the following constants: A = 0.40, B = 0.20, H = 1.20, f = 1.5, $k_1 = 2H^2$, $k_2 = 3 \times 10^6$ H, $k_3 = 48$ H, $k_4 = 3 \times 10^3$, $k_5 = B$, $k_6 = 0.5$ B, $k_7 = 8 \times 10^9$, $k_{-7} = 2 \times 10^{-2}$, and $k_8 = 2 \times 10^{-2}$. The initial conditions were set as follows: $[X] = 2 \times 10^{-7}$, $[Y] = 2 \times 10^{-6}$, $[Z] = 1 \times 10^{-4}$, $[P] = 1 \times 10^{-7}$, and $[U] = 1 \times 10^{-7}$. As a result, oscillation in the Br₂ concentration was observed (Figure S3).



Figure S3. Result of the numerical calculation using the modified Oregonator. The solid line indicates the Br_2 concentration, and the broken line indicates the oxidized catalyst.