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Noise-induced kinetic model for autonomous motion of the contact line in oil-water systems with chemical reactions

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A model for autonomous motion of the contact line of the oil-water interface along a solid surface is proposed. The present model is inspired by the spontaneous wave generation and the contact line motion of an oil-water interface composed of cationic surfactant and oil-soluble anions. The motion is created through wetting by an adsorption of surfactant followed by an autocatalytic process with a chemical reaction and also dewetting due to the desorption of the remaining monolayer. The wetting process is accelerated by the contact line motion itself through the convection-enhanced transport of reaction constituents, which is autocatalytic in nature. These processes are expressed by nonlinear time-evolution equations for the velocity and the amplitude. Following the model, the autonomous motion is essentially excitable, and hence the spatiotemporal pattern is of the noise-induced type. The present model explains well the diverse features of the experimental results with a few parameters.

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I. INTRODUCTION

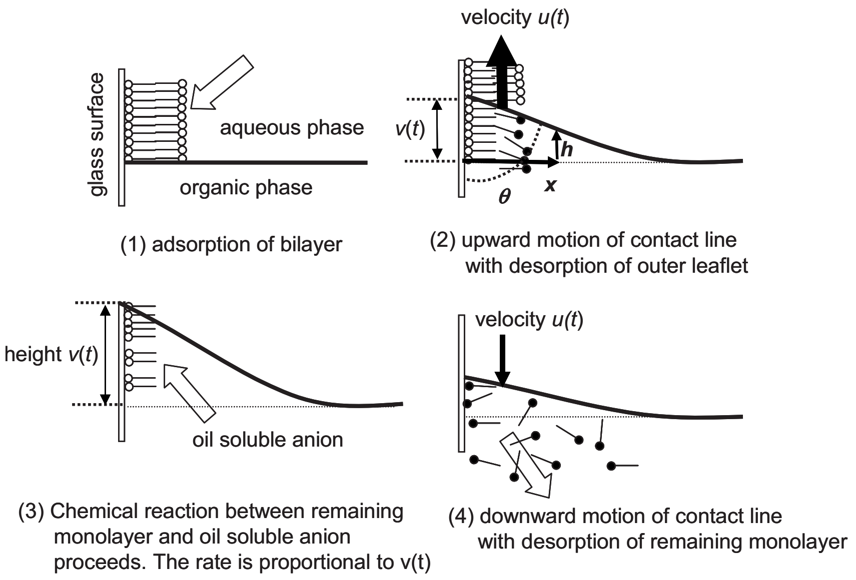
An oil-water interface with chemical reactions sometimes causes regulated autonomous motion such as wave rotation along a cylindrical sidewall [1–7] or translation or rotation of a droplet [8–11]. These are examples of systems which can turn chemical energy directly into work. Some of them have a chemosensitive nature, e.g., one can design a pendant drop which detects Ca^{2+} to move in a regulated manner [11]. Understanding autonomous motions is a typical issue in the spatiotemporal pattern formation field of nonlinear kinetics, and such chemosensitive motions may be used to design chemical systems which look like living matter. Therefore, the autonomous motions of the oil-water systems have been studied in detail over the past three decades [1–11].

One of the well-known oil-water interfaces was found by Dupeyrat and Nakache [1,2]. This system contains the cationic surfactant octadecyltrimethylammonium chloride $C_{18}TAC$ in the aqueous phase and oil-soluble anions in the organic phase. Polyiodide anion is a typical example. An outstanding transverse wave rotates along the vertical sidewall made of glass [4]. It is well accepted that the adsorption of $C_{18}TA^+$ onto a negatively charged glass surface plays a key role [6,7,9,10]. The electrostatic adsorption changes the hydrophobicity (hydrophilicity) of the glass surface which induces a wetting transition by the organic phase. The adsorption layer is then soaked in the organic phase. This enables the oil-soluble anion to react with the $C_{18}TA^+$, forming the adsorbed layer. This reaction causes desorption of the adsorbed layer which makes the glass surface hydrophilic again. This sequence of events repeats quasiperiodically [6,7,9,10]. Although the spatiotemporal pattern formation has been studied many times [1–10], a simple mathematical model which can describe the diverse features of the experimental observations has not been proposed yet. The mathematical modeling is not easy because the instability inherent in this phenomenon is unclear; a certain instability or autocatalytic process is necessary for such autonomous motion. Sumino *et al.* [9,10] proposed a mathematical model for the droplet translation of this oil-water system, which captures well the essential features of the regulated motion. However, the droplet is treated as an elementary moving object in this model, and hence the autocatalytic process contained therein cannot be directly applied to the autonomous motion of the contact line and to the wave generation.

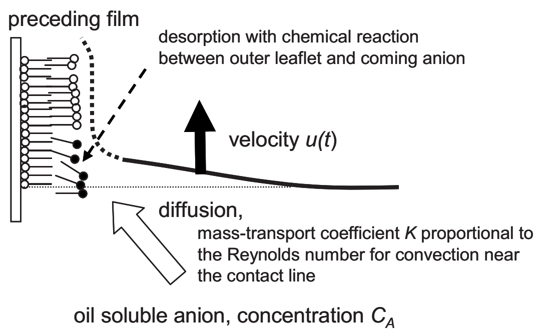
In this paper, we propose a simple mathematical model which can describe the autonomous motion of the contact line. The present model includes an instability mechanism which is deduced from the experimental observations mentioned above. The underlying physics are well described by the model, and the diverse features of the experimental results are well explained by setting a few parameters in this simple model. The parameter change for reproducing the experimental results reasonably corresponds to the variation in the experimental conditions. In this model, the autonomous motion of the contact line is not oscillatory but excitable. Thus, the spatiotemporal pattern is produced by a kind of noise-induced or stochastic kinetics [13]. Also at this point, a semiquantitative coincidence between the model and experiments is obtained.

II. MODEL

Figure 1(a) shows a schematic representation of the autonomous motion of the contact line along the glass surface. The $C_{18}TA^+$ cations are adsorbed on the surface as a bilayer, which is well established at the concentration beyond the critical micelle concentration [14]. Following a previous paper [7], the contact line moves upwards as it desorbs the outer leaflet. In this process, the desorption rate of the outer leaflet restricts the rate of the surface change from hydrophilic to hydrophobic. The desorption comprises two kinds of processes. One is the chemical reaction between the adsorbed $C_{18}TA^+$ and the oil-soluble anion in the organic phase. For a wetting process, we often consider the presence of a film preceding contact line [15]. Following this consideration, we assume that the adsorbed bilayer in the vicinity of the contact line is wetted by a thin layer of the organic



(a) periodic change in meniscus shape



(b) microscopic view for desorption of outer leaflet

FIG. 1. Schematic representation of contact line motion. (a) Each process constituting a periodic change, (b) microscopic view of chemical desorption of outer leaflet.

phase [Fig. 1(b)]. In the thin layer, the chemical reaction proceeds. Another rate controlling step in this process is the diffusion of the oil-soluble anion through the thin layer. The mass-transport coefficient to and within the thin layer strongly depends on the velocity of the contact line motion; strictly the Reynolds number of the oil phase near the contact line [16]. The considered scheme is illustrated in Fig. 1(b). The anion diffuses through the thin layer with a mass-transport coefficient K. Let us put the rate constant of the chemical reaction between the adsorbed $C_{18}TA^+$ and the anion k. Then, the desorption rate r_1 is expressed by [16]

$$r_1 = \frac{C_A}{\frac{1}{k} + \frac{1}{K}}. \tag{1}$$

Here, we assume that the adsorption density of $C_{18}TA^+$ is the saturation, and hence the desorption rate r_1 is dependent only on the anion concentration in the bulk organic phase, C_A. The mass-transport coefficient is determined by the convection near the contact line. Thus, we assume K is proportional to Re^{β}, where Re is the Reynolds number for the convection. Although the value of β is, for example, 0.83 [17], only its positive sign is important to grasp the essence. Thus, we postulate it to be unity. Since the density and the viscosity may be constant values, we may consider the Re number as proportional to the value of $|u|$ that is the absolute value of velocity of the contact line motion. Then, we obtain

$$r_1 = \frac{\kappa'|u|}{1 + \frac{|u|}{k'}}. \tag{2}$$

Here, k' and κ' are proportional to k and C_A, respectively.

The upward motion of the contact line remains at the $C_{18}TA^+$ monolayer soaked in the organic phase as shown in Fig. 1(a) part (3). This monolayer is adsorbed by the electrostatic interaction with the glass surface. Thus, the rate of the desorption by the reaction with the oil-soluble anion is relatively slow compared to the outer leaflet. Most simply, this slower process r_2 is expressed by

$$r_2 = \chi \int_0^t u\,dt. \tag{3}$$

Here, t is the time from the initial. Equation (3) means that the desorption rate is simply proportional to the length of the remaining monolayer soaked in the organic phase, which is a function of time. The downward motion of Fig. 1(a) part (4) is driven by the unstable contact between the hydrophilic surface and oil. Thus, the right-hand side of Eq. (3) may be proportional to the driving force of the downward motion of the contact line.

Following the theory of wetting [15], the force driving the contact line is determined by the difference in interfacial tensions between the water-glass and the oil-glass interfaces. In the present case, the difference varies with both the desorption of the outer leaflet and that of the remaining monolayer, and hence the nonzero desorption rate generates the driving force. Thus, we may consider that the driving force, which is equal to $m\,du/dt$, is expressed by

$$\frac{du}{dt} = -\mu u - \chi v + \frac{\kappa\Theta(u)u}{1+\dfrac{u}{k}} + \xi(t), \tag{4a}$$

$$\frac{dv}{dt} = u. \tag{4b}$$

The estimation of the mass m of the moving portion is difficult, and we postulate a constant value for it. The proportional constant κ' and χ are scaled by m, and the scaled values are newly defined as κ and χ. The k' value is rewritten as k. The first term on the right-hand side of Eq. (4a) represents the viscous drag force. The $\Theta(u)$ denotes the Heaviside step function; the fast desorption process of the outer leaflet mentioned above operates only for the upward motion of Fig. 1. The $|u|$ in Eq. (2) can be replaced by u for the presence of $\Theta(u)$. A term representing random noise $\xi(t)$ is present since the Marangoni effect at the oil-water interface and/or the contact line motion at other places around the observed point perturb the dynamics. The presence of $\xi(t)$ is essentially important as discussed later.

III. NUMERICAL CALCULATION

Numerical calculation of Eq. (4a) and (4b) is carried out with the fourth-order Runge-Kutta method for simultaneous differential equations. The time step of the integration is small enough that the calculated result does not depend on the time step within a three digit number.

Ignoring the effect of $\xi(t)$, Eq. (4a) and (4b) gives a stationary point $u=v=0$ which is stable for the fluctuation with the decrease in u and unstable for the opposite fluctuation. When a stationary point is chosen as the initial value, a positive value of $\xi(t)$ is responsible for a pulselike change in $u(t)$ and $v(t)$. Both quantities return to the stationary state via a single pulse. If $\xi(t)$ is always nonzero, the pulselike change constitutes a quasiperiodic oscillation in $u(t)$ and $v(t)$.

Figure 2 shows the calculated pattern of $u(t)$ and $v(t)$ for several sets of (μ,χ,κ) with $k=1$. When the glass surface is set perpendicular to the interface, the value of $v(t)$ represents the height of the contact line from the stationary value, $v=0$. We assume the following equation [15] representing the capillary-gravity balance for the oil-water interface to calculate the $\cos\theta(t)$,

$$x - x_0 = L\cosh^{-1}\left(\frac{2L}{h}\right) - 2L\sqrt{1-\left(\frac{h}{2L}\right)^2}. \tag{5}$$

Here, x, h, and $\theta(t)$ are defined as shown in Fig. 1(a) part (2). L stands for the capillary length, and x_0 is determined so as to make $h=v(t)$ at $x=0$. The change in $\cos\theta(t)$ is also shown in Fig. 2. Note that the pattern of $\cos\theta(t)$ is applicable to the vertical glass surface and that the others, $u(t)$ and $v(t)$, can be used independently of the geometry.

The result shown in Fig. 2 is calculated for sufficiently small $\xi(t)$, i.e., it is a random variable between -10^{-5} and 10^{-5}. This term corresponds to the random noise induced by the Marangoni effect of the oil-water interface and/or perturbations due to the contact line motion at other places. The third term on the right-hand side of Eq. (4a) corresponds to the autocatalytic process. Thus, a larger κ value increases the amplitude $v(t)$, which is shown in Figs. 2(a) and 2(c). Infinite autocatalytic growth is inhibited by $-\chi v$ of Eq. (4a), and hence the amplitude $v(t)$ is smaller with the increase in χ [see Figs. 2(a) and 2(b)]. The stronger the inhibition effect is, the faster the point (u,v) in the phase space returns to the stationary point. Thus, a larger χ value increases the frequency of the pulses. The infinite autocatalytic growth is also inhibited by $-\mu u$ of Eq. (4a). As shown in Figs. 2(a) and 2(d), a decrease in μ results in an increase in the oscillation amplitudes. This means that a lower viscosity allows a larger value of $u(t)$, $v(t)$ and a faster motion (higher frequency).

The chemical reaction rate constant k affects the pattern as shown in Figs. 3 and 2(a). The autocatalytic nature arises from the dependency of r_1 on $u(t)$. This dependency is outstanding only when the whole reaction rate r_1 is diffusion limited. When the chemical reaction rate constant k is too small, the autocatalytic mechanism does not work well; the whole reaction rate is controlled by the chemical reaction rate k itself. Therefore, one can expect that the pulse of $u(t)$ and $v(t)$ is more outstanding with the increase in k. This is clearly shown in Figs. 2(a) and 3.

Figure 4 shows the dependency of the random noise on the calculated patterns. When $\xi(t)=0$, $u(t)$ and $v(t)$ are always zero as far as the initial condition is chosen for $u=v=0$. Figures 2(a) and 4 indicate that the average frequency of the pulses increases with increasing $\xi(t)$. The point (u,v) in the phase space returns to the stationary point via a closed trajectory. The point in the phase space can go on its next cycle only when the distance between the point and the stationary one is less than the maximum value of $\xi(t)$. Consequently, a larger value of $\xi(t)$ rushes the point to the next cycle, which results in the higher frequency. However, an extremely high noise level violates the quasiperiodicity, and a randomlike pattern appears. An appropriate noise intensity is necessary for the quasiperiodic motion of the contact line. The present model is a kind of noise-induced or stochastic kinetics [13].

IV. COMPARISON WITH EXPERIMENTAL RESULTS

In the present model, the electrostatic interaction between the glass surface and $C_{18}TA^+$ affects the value of χ, since the

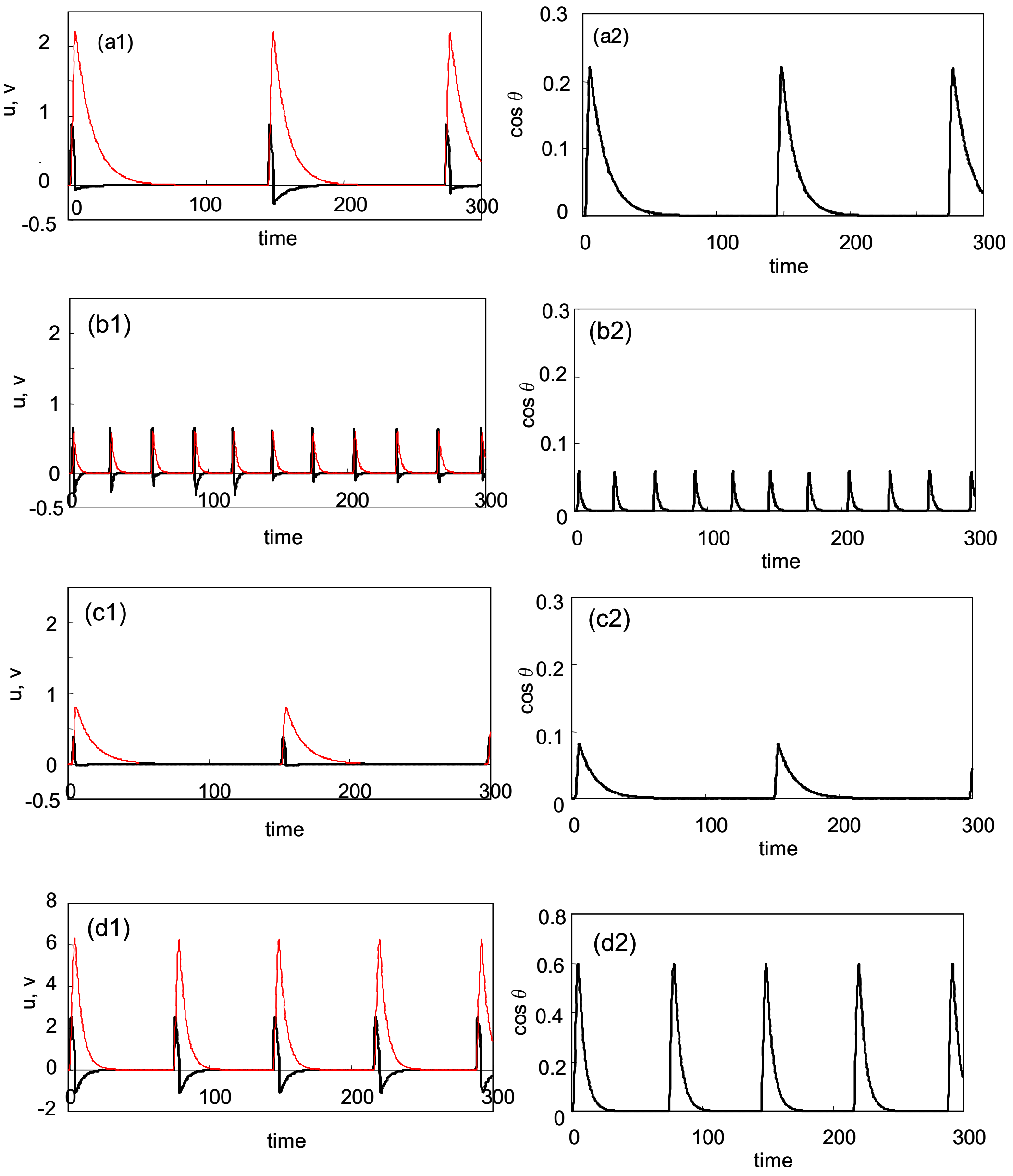


FIG. 2. (Color online) Calculated $u(t)$ [upward and downward spikes (dark curve) on the left-hand side], $v(t)$ [upward spikes (light curve) on the left-hand side], and $\cos\,\theta(t)$ (right-hand column) are shown for four kinds of parameters: (a) $\mu=10$, $\chi=1$, $\kappa=20$; (b) $\mu=10$, $\chi=5$, $\kappa=20$; (c) $\mu=10$, $\chi=1$, $\kappa=15$; (d) $\mu=5$, $\chi=1$, $\kappa=20$. Other parameters are $k=1$ and $-10^{-5}<\xi<10^{-5}$ for all cases. Quantities of the abscissa and the ordinate are dimensionless.

strong electrostatic interaction makes the desorption rate of the remaining monolayer slower. The stronger interaction is accomplished by the aqueous phase with higher *p*H; the glass surface is charged more negatively with higher *p*H [14]. In the present oil-water system, the amplitude of the rotating wave, which reflects the amplitude of the contact line motion, increases with increasing *p*H [7]. This can be understood by the increase in the amplitude of $v(t)$ with decreasing χ as shown in Fig. 2 [see Figs. 2(a) and 2(b)].

The amplitude of the rotating wave or the contact line motion is larger when the concentrations of $C_{18}TA^{+}$ and anions are higher [4]. The increase in the concentration corresponds to the increase in κ since it includes the anion concentration C_A. Please note that we assume saturation of the adsorbed $C_{18}TA^{+}$. Figure 2 indicates that the amplitude of $v(t)$ increases with the increase in κ, which agrees with the experimental tendency [see Figs. 2(a) and 2(c)].

Recently, the authors examined the role of the anions and obtained the following results [12]: The chemical reaction between the anion and $C_{18}TA^{+}$ takes place both at the oil-water interface and at the contact line on the glass surface. The former generates a spontaneous convection due to the Marangoni instability, and the latter causes a periodical motion of the contact line. Cooperation between them produces the outstanding wave propagation. The time course of $\gamma\cos\,\theta$ was reported [12] and the interfacial tension γ does not change strongly [6]. Thus, we can compare the experimental results of $\gamma\cos\,\theta$ with the calculated $\cos\,\theta$. The

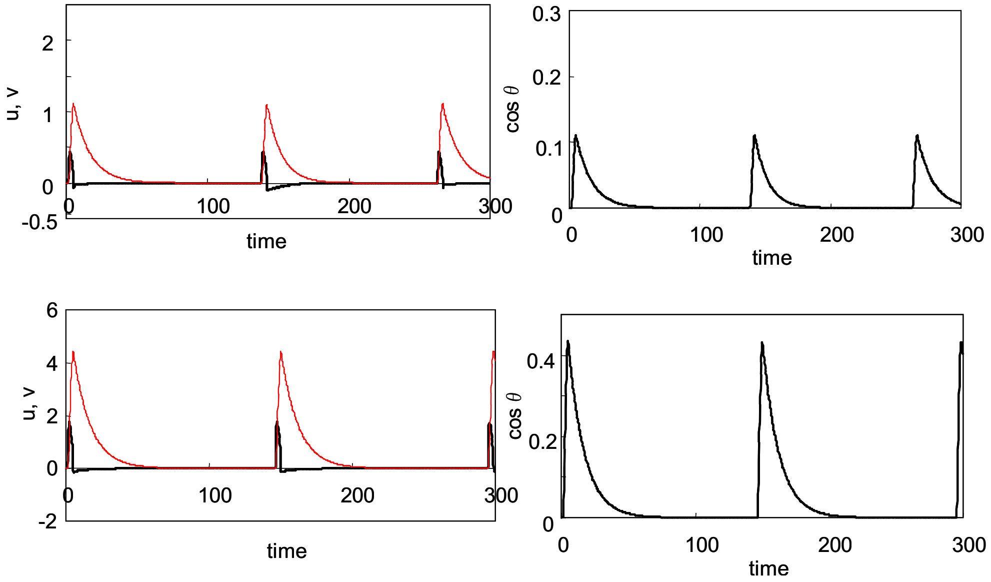


FIG. 3. (Color online) Dependency of calculated $u(t)$ [upward and downward spikes (dark curve) on the left-hand side], $v(t)$ [upward spikes (light curve) on the left-hand side], and cos $\theta(t)$ (right-hand column) on the reaction rate constant, $k=0.5$ (upper) and $k=2$ (lower). Other parameters are $\mu=10$, $\chi=1$, $\kappa=20$, $-10^{-5}<\xi<10^{-5}$. Quantities of the abscissa and the ordinate are dimensionless.

change in γ cos θ obtained in the experiment of Ref. [12] is summarized in Fig. 5. Based on the results, more hydrophobic anion bis(2-ethylhexyl)phosphate DEHP$^-$ (or I_3^-), mainly induces the contact line motion, and more hydrophilic anion phenylborate PB$^-$ (or I^-) causes the Marangoni instability at the oil-water interface. We may consider that the increase in PB$^-$ concentration corresponds to the increase in $\xi(t)$. The pattern of the calculation with intermediate noise intensity [Figs. 4(a) and 4(b)] agrees well with the experimental result of the PB-free interface, at the top of Fig. 5. The increase in PB$^-$ concentration clearly introduces a randomness in the pattern (the bottom of Fig. 5), which is well reproduced by the calculation with increased $\xi(t)$ [Fig. 4(c)]. The pattern calculated for the intermediate $\xi(t)$ [Fig. 4(b)] is also similar to the pattern observed by Magome and Yoshikawa for iodide-anion system (Fig. 1 in Ref. [8]). In the present oil-water system, the wave generation sometimes failed when contact between a flat oil-water interface and the glass surface was made without some perturbation or turbulence due to pouring the solution [7]. This empirical fact suggests that a certain amount of noise is necessary for the generation of the autonomous motion. This is well reproduced by the present model.

In order to compare the calculated $v(t)$ with the experiment, we measured the oscillatory change in an oil droplet in C$_{18}$TAC-containing aqueous phase. As reported previously [12], the droplet exhibits an oscillatory shape change between hemispherical and flattened shapes when the organic phase includes 100 m*M* DEHPA. (See inset of Fig. 6.) The motion was analyzed by high speed video at 125 frames/s. Figure 6 shows the positional change of the droplet periphery. The pattern can directly be compared to the $v(t)$, since the $v(t)$ is not affected by gravity. The pattern is very similar to Fig. 4(a) or Fig. 4(b). This indicates that the noise intensity to reproduce the $v(t)$ also generates a similar pattern to the experimentally observed cos θ of PB-free system. This

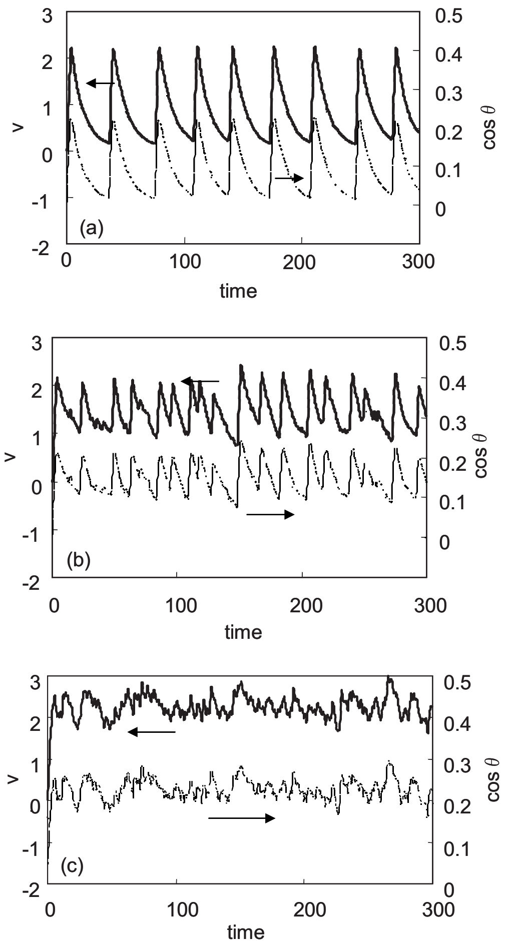


FIG. 4. Effect of noise intensity on pattern of $v(t)$ and cos $\theta(t)$: $-0.1<\xi<0.1$ (a), $-1.0<\xi<1.0$ (b), and $-3.0<\xi<3.0$ (c). Other parameters are $\mu=10$, $\chi=1$, $\kappa=20$, and $k=1$. Quantities of the abscissa and the ordinate are dimensionless.

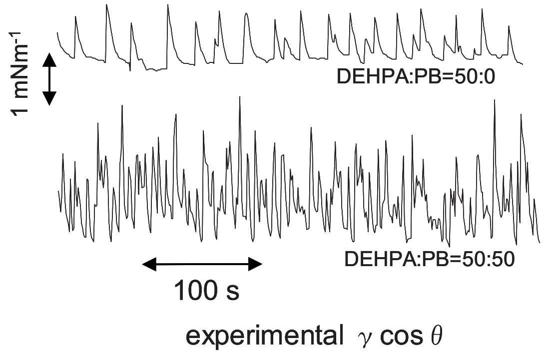


FIG. 5. Experimentally observed $\gamma \cos \theta$ (Ref. [12]). Concentrations of $C_{18}TAC$, bis(2ethylhexyl)phosphoric acid (DEHPA), and phenylboronic acid (PB) are 1.15 m*M*, 50 m*M*, and 0 m*M*, respectively, for DEHPA:PB=50:0. They are 1.15 m*M*, 25 m*M*, and 25 m*M*, respectively, for DEHPA:PB=50:50.

result indicates that the present model explains well the contact line motion.

The present model is not sufficient to express the wave rotation along the glass wall. For this calculation, the coupling or the interaction of the oscillators at different places should be taken into account. Although the interaction or coupling is probably caused by the increased interfacial area due to an irregular growth of the aligned oscillators, this supposition is unconfirmed at present. However, if the oscillatory change in $v(t)$ is superposed on the translation (traveling) along the glass surface, the pattern of $v(t)$ shown in Figs. 2 and 3 may be regarded as the wave pattern. The earlier change in the oscillation amplitude $v(t)$ becomes the front of the traveling wave. Examples of such wave patterns are shown in Fig. 7(a) with the parameters for Fig. 2. Kai *et al.* [4] show an example of the experimental pattern in an iodide anion system (Fig. 4 of Ref. [4]). We can reproduce a quite similar pattern by setting the parameters appropriately, as shown in Fig. 7(b).

Despite its simplicity, the present model can explain many aspects of the spatiotemporal pattern of the oil-water system.

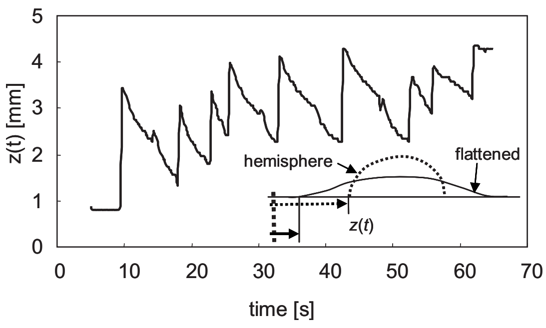


FIG. 6. Time course of distance from a fixed point to the droplet periphery, $z(t)$ as shown in the inset. Concentrations of $C_{18}TAC$ and DEHPA are 1.15 m*M* and 100 m*M*, respectively. Inset is a schematic illustration of change in the droplet shape. The droplet (100 μl) changes its shape without a significant translation. The details are reported elsewhere [12].

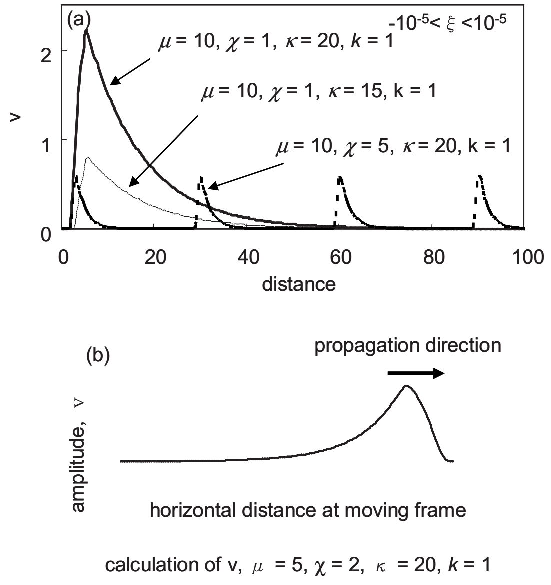


FIG. 7. Pattern of traveling wave simply estimated by the $v(t)$ value. The abscissa is simply estimated by the time (the abscissa of Fig. 2 or Fig. 3) multiplied by the traveling velocity. Since we assume a constant traveling velocity, the time can be equal to the distance in an appropriate unit. Quantities of the abscissa and the ordinate are dimensionless. (a) Pattern of $v(t)$ for parameters shown in Fig. 2. (b) Parameters are chosen for reproducing the experimental result of Fig. 4 in Ref. [4].

V. CONCLUSIONS

A simple model which can explain the contact line motion along a solid surface is proposed. The autonomous motion of an oil-water interface consisting of cationic surfactant and oil-soluble anions is well explained by the model. The motion consists of a bilayer adsorption of the surfactant on the solid surface, of an autocatalytic wetting with chemical desorption of the outer leaflet, and of a dewetting of the remaining monolayer with chemical reaction. These processes are expressed by a set of nonlinear differential equations. They have a stationary point which is unstable under the presence of noise or perturbation. The noise corresponds to the Marangoni effect at the oil-water interface and/or the contact line motion at other places near the calculated point. Despite its simplicity, the model can explain many aspects of the experimental results by setting a few parameters appropriately. The change in the parameters reasonably corresponds to that in the experimental conditions. The time course of experimental cos θ, the effect of the Marangoni instability on it and the geometry of the traveling wave are well reproduced by the present model.

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