Multiple Autonomous Motions Synchronized with Complex Formation

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The characteristic motion of a 1,10-phenanthroline grain on an $FeSO_4$ aqueous phase was investigated as a simple example of an autonomous motor. The uniform motion of the grain changed to intermittent motion (periodic change between motion and rest) and its period and resting time increased depending on the concentration of $FeSO_4$ (C_{FeSO_4}). However, this intermittent motion reverted to uniform motion and the velocity increased with a further increase in C_{FeSO_4}. The nature of this characteristic motion depending on C_{FeSO_4} is discussed in relation to the surface tension, which depends on surface concentration of surface active layer composed of 1,10-phenanthroline and a tris(1,10-phenanthroline) complex as the driving force.

1. Introduction

According to chemical kinetics, the concentrations of reactants and products can be temporally expressed by ordinary differential equations; that is, there is no information regarding the space for the reaction system. This suggests that chemical reactions can be generally considered to progress only in scalar variables under isotropic and linear conditions. On the other hand, according to the Curie−Prigogine theorem, scalar variables cannot couple with vector values under isotropic conditions.[1,2] This suggests that the introduction of anisotropic and nonequilibrium conditions can induce a controllable vectorial process in a reaction field.[3−5] Several autonomous motors and actuators have been investigated under conditions of chemical nonequilibrium.[4−12] We have been studying the vector process and mode changes in camphor motion as a simple autonomous motor that can adapt to internal (mass and shape of the camphor) and external (shape and size of the cell, and pH of the aqueous phase) nonequilibrium and anisotropic environments. The essential features of this self-motion can be reproduced by a computer simulation.[13−16]

In the present study, a 1,10-phenanthroline grain on an $FeSO_4$ aqueous phase was investigated as a novel autonomous motor. When the concentration of $FeSO_4$ (C_{FeSO_4}) is low enough, the uniform motion of the grain was observed. With the increase in C_{FeSO_4}, the uniform motion changed to intermittent motion (periodic change between motion and rest) and its period and resting time increased. However, this intermittent motion reverted to uniform motion and the velocity increased with a further increase in C_{FeSO_4}. The mechanism of this characteristic motion depending on C_{FeSO_4} is discussed in relation to the surface tension, which depends on the concentration of a surface active layer composed of 1,10-phenanthroline (phen) and a tris(1,10-phenanthroline) and iron complex ($[Fe(phen)_3]^{2+}$, ferroin) as the driving force and the solubility of ferroin in the aqueous phase. We believe that the various natures of self-motion will be designed under nonequilibrium and anisotropic conditions.

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2. Experimental Section

All chemicals were analytical grade reagents and used without further purification. Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water 6.3, resistance >20 MΩ). A solid disk of 1,10-phenanthroline (diameter 1 mm, thickness 0.5 mm, mass 0.6 mg) was prepared using a pellet die set for FTIR. Twenty milliliters of $FeSO_4$ aqueous solution of different concentrations was poured into a glass Petri dish (inner diameter 50 mm) as an aqueous phase (depth 10 mm). The temperature of the water cell was adjusted to 293 ± 1 K with a thermoplate (TP-80, AS ONE Co. Ltd., Japan). The movement of the phenanthroline disk was monitored with a digital video camera (SONY DCR-VX700, minimum time resolution 1/30 s) and then analyzed by an image-processing system (Himawari, Library Inc., Japan). The surface tension at the air/water interface was measured by the standard Wilhelmy method.

3. Results

Figure 1 shows (1) snapshots for (a) uniform motion ($C_{FeSO_4} = 0$ mmol L^{-1}), (b) intermittent motion ($C_{FeSO_4} = 5$ mmol L^{-1}), and (c) uniform motion ($C_{FeSO_4} = 100$ mmol L^{-1}) in self-motion of the phenanthroline disk, and (2) the time variation of its velocity. In uniform motion, a red-colored layer (darker area as seen in Figure 1b,c), which was composed of ferroin, remained on the path of the disk. In intermittent motion, the density of the red-colored layer around the disk increased in the resting state, but the resting state changed to rapid motion when the density of the red-colored layer reached a critical value, as seen in Figure 1b.

Figure 2 shows a mode diagram of the self-motion of the phenanthroline disk depending on C_{FeSO_4}. The velocity of uniform motion decreased with an increase in C_{FeSO_4}, and uniform motion changed to intermittent motion (periodic change between motion and rest) at $C_{FeSO_4} = 3$ mmol L^{-1}. If the velocity of the disk was less than 1 mm s^{-1} and the resting time in intermittent motion was greater than 1 min, we considered the motion to be ambiguous. The frequency of intermittent motion decreased and the resting time increased with a further increase in C_{FeSO_4}, and the phenanthroline disk almost settled at C_{FeSO_4}

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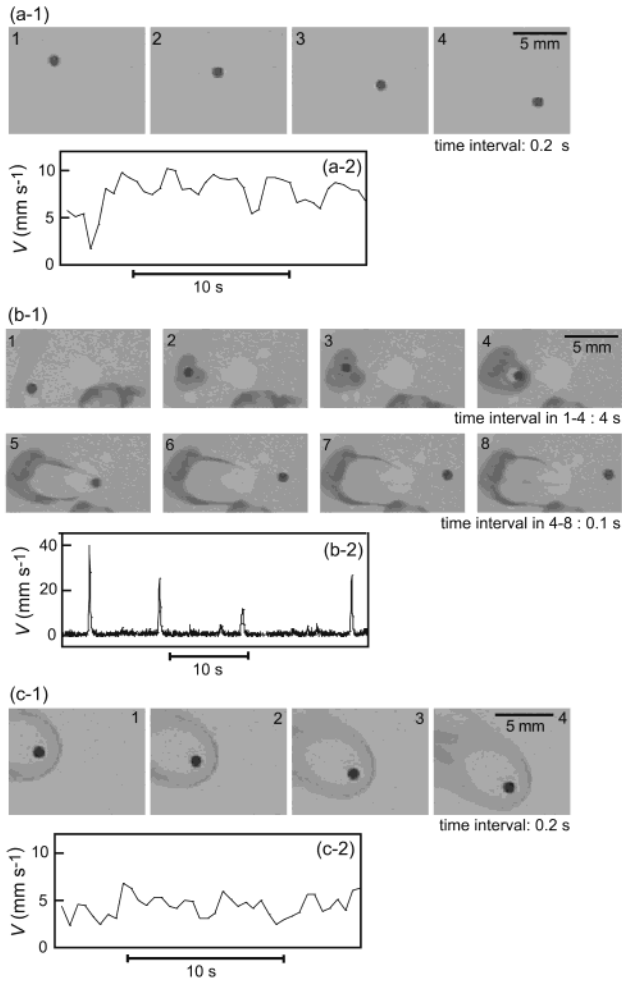

Figure 1. (1) Snapshots of the self-motion of a phenanthroline disk on an $FeSO_4$ aqueous solution at different concentrations ((a) 0, (b) 5, and (c) 100 mmol L^{-1}) (top view). (2) Time variation of the velocity of the phenanthroline disk.

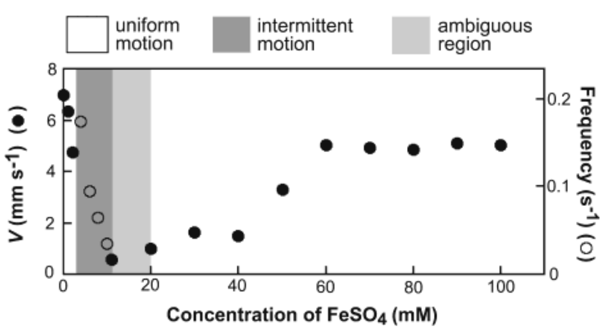

Figure 2. Mode of phenanthroline motion depending on C_{FeSO_4}, the velocity of uniform motion ($0 \leq C_{FeSO_4} \leq 2$, $30 \leq C_{FeSO_4} \leq 100$ mmol L^{-1}) including the ambiguous region ($11 \leq C_{FeSO_4} \leq 20$ mmol L^{-1}), and the frequency of intermittent motion ($3 \leq C_{FeSO_4} \leq 10$ mmol L^{-1}).

= 10 mmol L^{-1}. However, uniform motion recurred above $C_{FeSO_4} = 20$ mmol L^{-1}, and the velocity increased with a further increase in C_{FeSO_4}.

Figure 3 shows the dependence of the surface tension of the phenanthroline layer on the distance from its center (d) in the steady state. In this experiment, a phenanthroline disk (diameter 3 mm) was fixed to a platinum wire (diameter 0.5 mm) and then attached to the water surface. The surface tension remained at 72 mN m^{-1} for $d > 15$ mm, but clearly decreased for $d < 10$ mm.

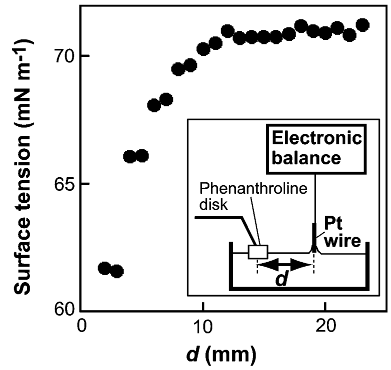

Figure 3. Dependence of the surface tension of the phenanthroline layer on the distance from its center at the steady state ($C_{FeSO_4} = 0$).

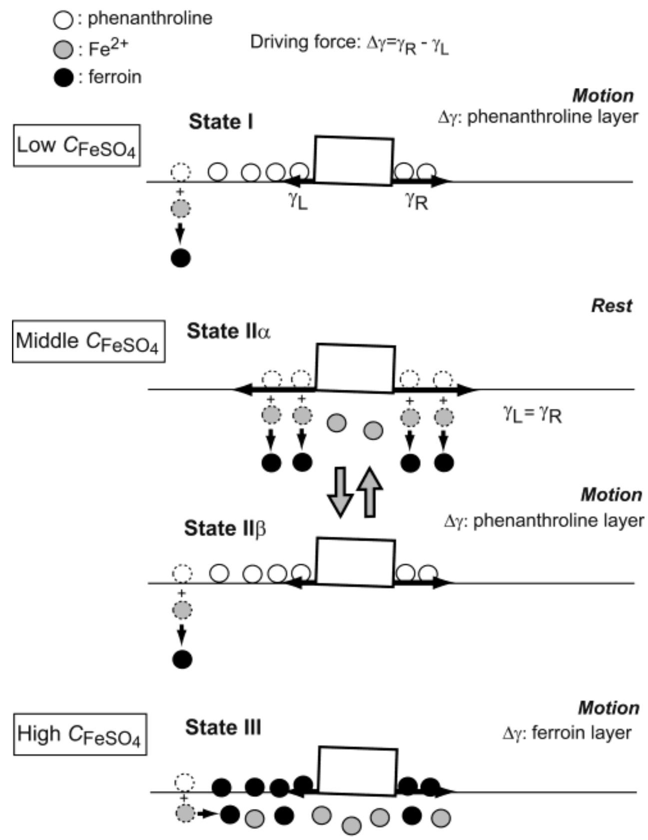

Figure 4. Schematic representation of the mechanism of the phenanthroline motion. States I, II, and III correspond to uniform motion at $0 \leq C_{FeSO_4} \leq 2$ mmol L^{-1}, intermittent motion at $3 \leq C_{FeSO_4} \leq 10$ mmol L^{-1}, and uniform motion at $30 \leq C_{FeSO_4} \leq 100$ mmol L^{-1}, respectively. States IIα and IIβ correspond to rest without a driving force and motion driven by the surface tension, respectively.

4. Discussion

On the basis of the experimental results and related papers on self-motion,[13-17] we can discuss the mechanism of the self-motion of a phenanthroline disk on an aqueous surface, as shown schematically in Figure 4. The direction of the motion is thought to depend on the initial floating state of the disk. Uniform motion at $C_{FeSO_4} < 3$ mmol L^{-1} is due to the successive formation of a phenanthroline layer, which plays an important role as the driving force within $d < 10$ mm around the solid, as suggested in Figure 3 (state I in Figure 4).

The intermittent motion at $3 \leq C_{FeSO_4} \leq 10$ mmol L^{-1} may be induced by the following mechanisms. Insoluble phenanthroline molecules, which develop from its solid, immediately form soluble ferroin (3 phen + $Fe^{2+} \rightarrow [Fe(phen)_3]^{2+}$) in the subphase (around the air/aqueous interface) (state IIα). This ferroin is surface inactive because it has a concentration lower than 10 mmol L^{-1},[17] and therefore the phenanthroline disk does not move. However, Fe^{2+} ions in the subphase run short because of the formation of ferroin, and a surface active phenanthroline layer then accumulates at the aqueous surface (state IIβ). Therefore, the phenanthroline disk moves to another location with sufficient Fe^{2+}. Thus, intermittent motion is generated by the repetition of states IIα and β. The increase in the resting time in intermittent motion with an increase in C_{FeSO_4} suggests that C_{FeSO_4} in the resting state is sufficient to play a role in ferroin complex formation, while it is insufficient in the moving state.

Above 30 mmol L^{-1} $FeSO_4$, a ferroin layer with a high concentration is produced around the phenanthroline disk. The surface tension decreases with an increase in the concentration of ferroin over 10 mmol L^{-1},[17] and therefore the uniform motion at $C_{FeSO_4} > 30$ mmol L^{-1} may be driven by the ferroin layer which is successively supplied by complex formation between phenanthroline and Fe^{2+} (state III). In fact, a red-colored ferroin layer remains in the path of the phenanthroline disk, as seen in Figure 1c. The increase in the velocity of uniform motion depending on C_{FeSO_4} at $C_{FeSO_4} > 30$ mmol L^{-1} is due to the salt precipitation of $FeSO_4$. The solubility of ferroin in the water phase decreases with the concentration of inorganic ions, and therefore ferroin molecules tend to concentrate on the air/water interface and the concentration of ferroin increases with an increase in inorganic ions. When $CaCl_2$ was added to the aqueous phase, the intermittent motion at $C_{FeSO_4} = 5$ mmol L^{-1} changed to uniform motion accompanied by a ferroin layer.

5. Conclusion

The mode of self-motion of a phenanthroline disk was discussed in relation to the accumulation and development of a phenanthroline layer around the disk, which depended on surface tension as the driving force. A mode change from uniform to intermittent and back to uniform motion with the ferroin layer depending on C_{FeSO_4} is induced coupled with the kinetics of ferroin formation around the phenanthroline solid.

Our results suggest that we can design various types of self-motion that depend on the relationship between the concentration of the surface active layer and its surface tension, coupled with the chemical reaction (e.g., neutral reaction,[16] complex formation, and redox reaction of ferroin[18−20]), and change the vector and mode by introducing anisotropic conditions to the reaction field. These multiple autonomous motions can be seen in other systems if the surface tension and solubility in an aqueous phase change coupled with the complex formations and also chemical reactions.

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